

Charge Transport and Defects in Sulfur-Deficient Chalcogenide Perovskite BaZrS₃

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Exploring the conduction mechanism in the chalcogenide perovskite BaZrS₃ is of significant interest due to its potential suitability as a top absorber layer in silicon-based tandem solar cells and other optoelectronic applications. Theoretical and experimental studies anticipate native ambipolar doping in BaZrS₃, although experimental validation remains limited. This study reveals a transition from highly insulating behavior to *n*-type conductivity (approximately 100 S/cm) in BaZrS₃ thin films through annealing in an S-poor environment. BaZrS₃ thin films are synthesized via a two-step process: co-sputtering of Ba-Zr followed by sulfurization at 600 °C, and subsequent annealing in high vacuum. Ultraviolet-visible spectroscopy measurements reveal a red shift of approximately 100 meV in the band gap concurrent with sample-color darkening after vacuum annealing. The increase in defect density from the order of 10¹⁷ to 10²¹ cm⁻³ with vacuum annealing, coupled with the low activation energy (approximately 8 meV), and the *n*-type character of the defects, strongly suggests that sulfur vacancies (*V*_S) are responsible for the *n*-type doping, in agreement with theoretical predictions. Temperature-dependent Hall measurement shows that phonon scattering governs charge transport at room temperature in BaZrS₃ films and that S vacancies are shallow donor defects acting as a weak impurity metal. The shift of the valence-band maximum (VBM) with respect to the Fermi level, quantified by hard x-ray photoelectron spectroscopy (Ga K α , 9.25 keV), further corroborates the induced *n* type of conductivity in annealed samples. Our findings indicate that vacuum annealing induces *V*_S defects that dominate charge transport, resulting in *n*-type conductivity in BaZrS₃ under S-poor conditions. These discoveries will inform important design choices, such as selecting appropriate contact materials, for integrating BaZrS₃ into solar cell structures or other devices.

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I. INTRODUCTION

Chalcogenide perovskites are emerging as highly promising optoelectronic materials, exhibiting a tunable band gap ranging from 1.1 to 2.0 eV and an absorption coefficient in the order of 10⁵ cm⁻¹ within the visible

range of the solar spectrum [1–4]. As their name suggests, chalcogenide perovskites crystallize in the perovskite structure, characterized by the chemical formula *ABX*₃, where chalcogens (commonly S or Se) occupy the anion “X” site. The “A” site is typically filled by +2 charged cations (such as Ba, Sr, or Ca), while the “B” site hosts +4 charged cations (e.g., Zr or Hf), which compensate for the −2 charge of the chalcogen anions. Both theoretical and experimental research has focused on several perovskite chalcogenides, with BaZrS₃ standing out due to its high stability, the abundance of its constituent elements, and a near-optimal band gap for use as the top-cell active layer in silicon-based tandem solar cells [5–15].

Most studies in the literature emphasize process development and the optical properties of BaZrS₃

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[9,11,12,16–20], and less attention has been paid to charge transport behavior. Yet, understanding defect characteristics is crucial for optimizing device performance, ensuring controllability of doping, and minimizing unwanted recombination processes. Several theoretical studies suggest that BaZrS_3 can exhibit intrinsic p -type or n -type behavior depending on the thermodynamic growth conditions [21–24]. While defect ionization levels can vary across different works in the literature, collectively some key observations can be made: the S vacancy (V_S), Zr interstitial (Zr_i), and Ba interstitial (Ba_i), and Zr substituting Ba (Zr_{Ba}) are shallow donor defects, while the Zr vacancy (V_{Zr}), the Ba vacancy (V_{Ba}), and Ba substituting Zr (Ba_{Zr}) are shallow acceptor defects, and the S interstitial (S_i) is a deep acceptor defect. Note that these defects (except for S_i) are either resonant with the conduction band (CB) or valence band (VB), or require minimal energy for ionization. The recent theoretical study by Yuan *et al.* suggests that BaZrS_3 exhibits intrinsic n -type conductivity due to shallow V_S defect levels under sulfur-poor conditions, while it shows weak n -type (nearly intrinsic) conductivity in sulfur-rich conditions [24].

The transition level of the S_i acceptor defect, which is likely to form in sulfur-rich environments, is a deep defect, meaning that it has a low probability of ionizing and contributing holes to the VB. Therefore, achieving p -type conductivity in BaZrS_3 is challenging and even in sulfur-rich conditions, the material tends to exhibit weak n -type or nearly intrinsic behavior.

In this paper, the charge-transport properties of BaZrS_3 thin films synthesized under S-rich conditions are investigated as well as their evolution in vacuum annealing, which induces S-poor conditions. The films are synthesized by sputtering Ba+Zr followed by sulfurization in an S-rich atmosphere. The as-prepared films were highly insulating but developed n -type conductivity when subjected to postannealing in a vacuum. In accordance with theoretical expectations, combined with multiple characterization techniques, we conclude that sulfur vacancies are the most likely origin of n -type behavior.

II. EXPERIMENTAL

A Kurt J Lesker system having six magnetron sources, each containing 3-in. targets, was used to deposit the thin films. These were deposited at room temperature and at a pressure of 5 mTorr in an Ar atmosphere on a quartz substrate. First, a thin Zr interlayer was deposited to protect the substrate from reacting with Ba. Next, a Ba-Zr layer was co-sputtered, with a targeted stoichiometry of 1:1. Finally, a capping layer of SnS was applied to protect the Ba-Zr precursor during transport to the sulfurization furnace [11]. The sulfurization of the sputtered films was performed in a home-built tubular furnace in an Ar atmosphere. The sample and a sulfur source were placed in a graphite box

and a titanium boat, respectively, which were inserted into different locations along the temperature gradient of the tube furnace. The sample was maintained at 600 °C and the S source at 135 °C. All films were sulfurized at around $(7 \pm 2) \times 10^{-1}$ mbar. After thin-film preparation, samples were cut into square sections (8 mm $\times$ 8 mm to 10 mm $\times$ 10 mm) to be used in van der Pauw configuration for Hall measurements. These cut samples were then annealed in a vacuum-assisted tubular furnace ($<1 \times 10^{-6}$ mbar) to induce S-poor conditions. For this, samples were loaded into a ceramic boat inside a quartz tube. The annealing conditions were determined by initially testing a range of temperatures from 300 to 600 °C for 0.7 h, with significant changes in the film only observed at temperatures above 500 °C. The annealing duration was then varied between 0.7 and 2.1 h, with conductivity saturating after 1.4 h. Based on these findings, three specific annealing conditions were selected and labeled using the notation T - t , where T represents the temperature (°C) and t indicates the duration (h).

The phase purity and crystallinity were characterized before and after the annealing via X-ray diffraction (Empyrean). The film morphology and thickness were also examined using transmission electron microscopy (TEM; Titan Themis 200 FEI, equipped with a SuperEDS detector from Oxford). TEM lamellas were carefully prepared using a focused ion beam (FIB) in a StrataDB235 (FEI) and Crossbeam 550 (Zeiss) system, with final polishing conducted at an ion-accelerating voltage below 5 kV. Energy-dispersive spectroscopy (EDS) (Zeiss LEO 1550 SEM with an EDAX EDS) was used to analyze the chemical composition of the samples, while time-of-flight elastic recoil detection analysis (TOF ERDA) was used to determine depth-resolved compositional information. Transmittance and reflectance spectra were recorded in the wavelength range between 300 nm and 800 nm with a step resolution of 1.0 nm, employing a Lambda 950 double-beam UV–Vis–near-infrared (NIR) spectrophotometer equipped with an integrating sphere and a Spectralon reflectance standard. Room-temperature Hall measurements were carried out in van der Pauw configuration and a magnetic field of 1 T in an ezHEMS Hall setup by NanoMagnetics. Titanium-gold Ohmic contacts were deposited on the corners of the BaZrS_3 -quartz samples to facilitate electrical measurements. The Ohmic nature of the contacts was validated by a current sweep. To ensure data reliability, multiple samples were simultaneously annealed in a single run, each cut from the same BaZrS_3 film, and their electrical properties were measured. Seebeck measurements were performed in a home-built setup, with samples placed on Peltier elements. The voltage difference caused by temperature differences was measured at the two ends of the sample. The slope of the temperature difference ΔT versus the induced voltage V was calculated to obtain the Seebeck coefficient.

Temperature-dependent conductivity measurements were performed in van der Pauw configuration using a Quantum Design physical-properties measurement system (PPMS). A sweep of the magnetic field from +5 T to −5 T was done for resistivity measurements from 300 K to 10 K.

The TOF-ERDA measurements were performed on the 5-MV NEC-5SDH-2 tandem accelerator at Uppsala University, using a primary beam of 36 MeV $^{127}\text{I}^{8+}$ primary ions, incident at 67.5° with respect to the sample-surface normal. Recoils were detected at an angle of 45° relative to the path of the primary beam. The TOF-ERDA detector system consisted of a TOF telescope followed by a gas-ionization chamber, so that both the energy and TOF of the recoiled particles were recorded in coincidence [25]. Composition depth profiles from TOF-ERDA measurements were calculated using the POTKU software package [26]. XPS was utilized to identify the elemental composition and to investigate the electronic structure of the BaZrS₃ surfaces. Additionally, XPS was employed to determine the VBM positions with respect to the Fermi level for all the samples, facilitating the study of the doping type before and after annealing. Since XPS measurements require good conductivity of the samples, BaZrS₃ films were separately prepared on a Si substrate and annealed along with the quartz samples. XPS measurements were acquired at the Kai-Siegbahn laboratory at Uppsala University, provided by two monochromatic sources and the hemispherical electron analyzer EW4000 (Scienta Omicron). The spectra were measured by Al K α (1.487 keV) and Ga K α (9.25 keV) x rays, which allowed us to probe different depths into the surface (Al K α , <1 nm; Ga K α , approximately 10 nm). Before the measurements, the samples were mounted on a carbon tape on the sample holder, together with a gold foil for the energy calibration of the spectra, and the conductivity of the samples was ensured by a multimeter. During acquisition, the pressure of the main chamber was $<1.0 \times 10^{-9}$ mbar. The surveys at Al K α and Ga K α were acquired with a pass energy of 500 eV and a step size of 0.5 eV. The S 1s core level and VB spectra measured at Ga K α photon energy were collected with a pass energy of 300 eV and with an energy step size of 0.1 eV. All the XPS spectra were energy calibrated to the Fermi level by measuring an Au foil and setting the binding-energy position of Au 4f_{7/2} at 84.0 eV. The S 1s peak position for all the samples was achieved by fitting the core-level spectra following the least-squares-error method, while the position of the VBM for the as-prepared sample was determined by a linear intersection of the VB edge with respect to the background.

III. RESULTS AND DISCUSSION

A. Structural properties

Figure 1(a) shows grazing-incidence XRD (GIXRD) scans of as-prepared and annealed BaZrS₃ thin films at

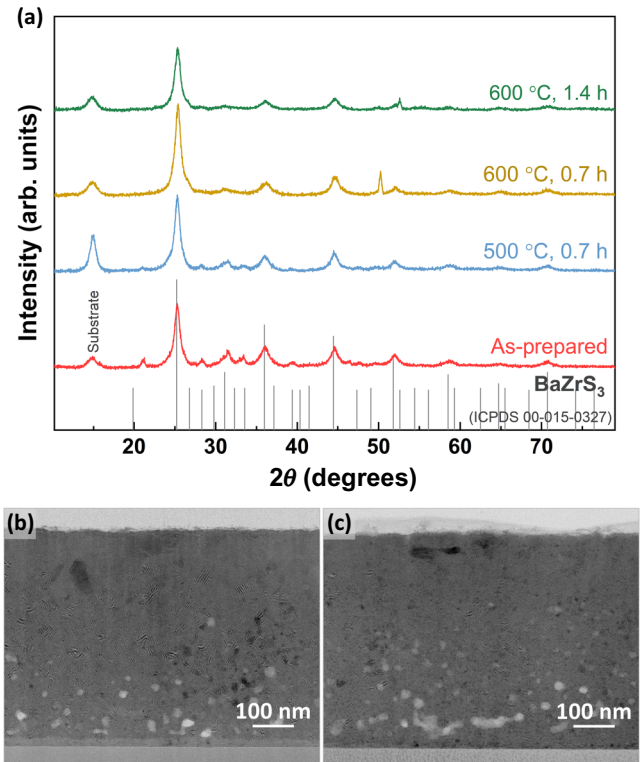


FIG. 1. (a) Grazing-incidence XRD (GIXRD) scans of as-prepared and annealed BaZrS₃ thin films, (b),(c) Cross-section TEM images of as-prepared and annealed (600-0.7) BaZrS₃ thin films, respectively.

1° incident angle in the 2θ range of 10° to 80° . The drop lines correspond to standard BaZrS₃ powder (ICPDS 00-015-0327). The diffraction patterns confirm that the films are polycrystalline and dominated by the BaZrS₃ phase, with no evidence of secondary phases. Notably, vacuum annealing at 500°C has little effect on the diffraction pattern, while annealing at 600°C results in only a slight reduction in some of the minor reflections. Overall, the BaZrS₃ phase remains stable and dominant in all cases. In Figs. 1(b) and 1(c), we show cross-section TEM images of as-prepared and annealed (600-0.7) BaZrS₃ films. A dense microstructure with a thickness of approximately 450 ± 30 nm is observed, with no significant morphological differences due to annealing. Surface SEM images in Fig. S1 of the Supplemental Material [27] further confirm the continuity and uniformity of the films. Together, these observations indicate that the films are dense, structurally uniform, and retain their integrity following vacuum annealing.

B. Optical properties

The as-prepared BaZrS₃ thin films exhibited a distinct orange hue on the transparent substrate, which shifted to a dark brown following annealing, as shown in the inset of Fig. 2. Optical images of all four samples are provided in

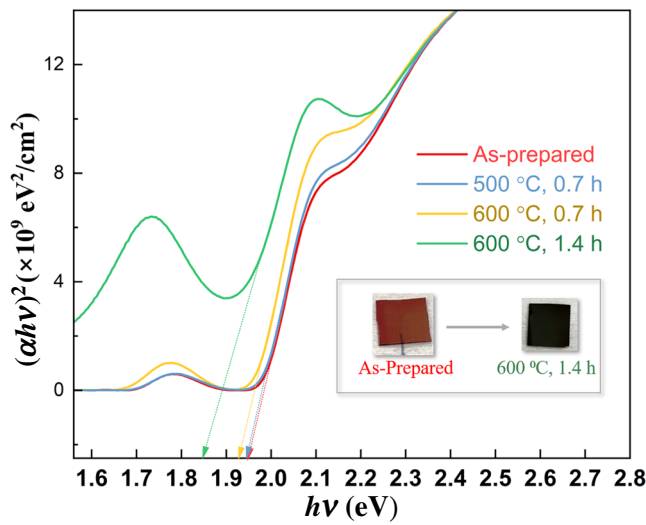


FIG. 2. The Tauc plot (solid lines) of $(\alpha h\nu)^2$ versus $h\nu$ for as-prepared and annealed BaZrS₃ thin films. The inset shows optical images of the as-prepared and annealed samples (600-1.4).

Fig. S2 in the Supplemental Material [27]. The change in the color of the films suggests alterations in the electronic structure, potentially driven by variations in the defect chemistry or stoichiometry. The optical response of the films further confirms these changes. In Fig. 2, we show the Tauc plot of the annealed and as-prepared films. The plot is constructed by plotting $(\alpha h\nu)^2$ versus $h\nu$, where α is the absorption coefficient (cm^{-1}) and $h\nu$ is the photon energy (eV) [28]. A linear region is observed in all four samples and its extrapolation to the X axis yields a band-gap energy of 1.95 eV for as-prepared and 500-0.7, 1.92 eV for 600-0.7, and 1.84 eV for 600-1.4. Tauc-plot analysis indicates that BaZrS₃ is a direct band-gap material with a high absorption coefficient in the order of 10^4 cm^{-1} in the visible range of the spectrum. The extracted band-gap values fall in the range of 1.8–1.9 eV, which aligns well with previously reported literature values [21–24,29,30]. It is observed that the band gap decreases as the annealing temperature and duration increase. The sample annealed at 600-1.4 exhibits very high absorbance for all wavelengths, and visibly also appears opaque (see Fig. S2 in the Supplemental Material [27]). All samples have a consistent absorption peak beyond the band-to-band transition (at low energy values). The origin of this peak is not clear at this point. Possible reasons might be the transition originating from the interface between the film and the substrate, the presence of defects, or the presence of secondary phases of the Ba-Zr-S system that are present in small quantities but not observable in structural characterization [28,31,32]. Nevertheless, a red shift is observed in the adsorption edge post annealing.

Band-gap shifts and associated color darkening with vacuum annealing are reportedly observed in metal oxides

when annealed in a vacuum or oxygen-deficient environment [33–35]. The generation of oxygen vacancies is the primary reason for such behavior, also altering the electrical properties, as films become more conductive with annealing due to an increase in electron concentration with oxygen-vacancy defects [36,37]. Given that all of the above observations are consistent with the findings in BaZrS₃ thin films, a similar phenomenon is hypothesized to be occurring in these films. Annealing in vacuum induces S-vacancy defects (V_S) with increasing concentration as the annealing temperature and duration are increased. The increased number density of sulfur vacancies leads to the delocalization of impurity states, which, due to the shallow nature of the defects, start to overlap with the VB edge. This would result in the red shift of the absorption edge observed in Fig. 2. The creation of S vacancies (donor defects, $V_S^{\bullet\bullet}$) with their shallow defect level should also manifest in the electrical properties, inducing the n type of conductivity in the film.

C. Electrical properties

The as-prepared samples exhibited high resistivity, making it challenging to measure their electrical properties. However, the vacuum postannealing led to a significant increase in conductivity. Four-probe measurements indicated conductivity on the order of 0.1 and 100 S/cm for the samples with the lowest (500-0.7) and highest (600-1.4) thermal budget, respectively. Furthermore, the Hall-effect measurement displayed a negative Hall coefficient, confirming n -type conductivity. To verify this, the Seebeck coefficient of each sample was also measured (see Fig. S3 in the Supplemental Material [27]). The results from both Seebeck and Hall measurements consistently indicated n -type conductivity in the films. The variation in carrier concentration and mobility with different annealing parameters was also examined by Hall measurement.

In Fig. 3(a), we present the carrier concentration of films annealed under different conditions. The vertical error bars in the graphs represent the measurement uncertainty, accounting for repeatability and instrumental error. The charge carrier concentration is observed to be increasing with increasing annealing temperature and duration. The carrier (electron) concentration directly correlates with the number density of defects (donors) that are ionized at room temperature. This suggests that annealing generates positively charged donor defects in the films, inducing n -type conductivity, with the density of ionized defects rising as the annealing conditions intensify. The Seebeck coefficient also shows similar results (see Fig. S3 in the Supplemental Material [27]) and is found to be decreasing with annealing temperature and duration. It is important to note that beyond a certain point, the carrier concentration begins to saturate, approaching the metallic regime (approximately 10^{22} cm^{-3}) [Fig. 3(a)]. Simultaneously, the films become

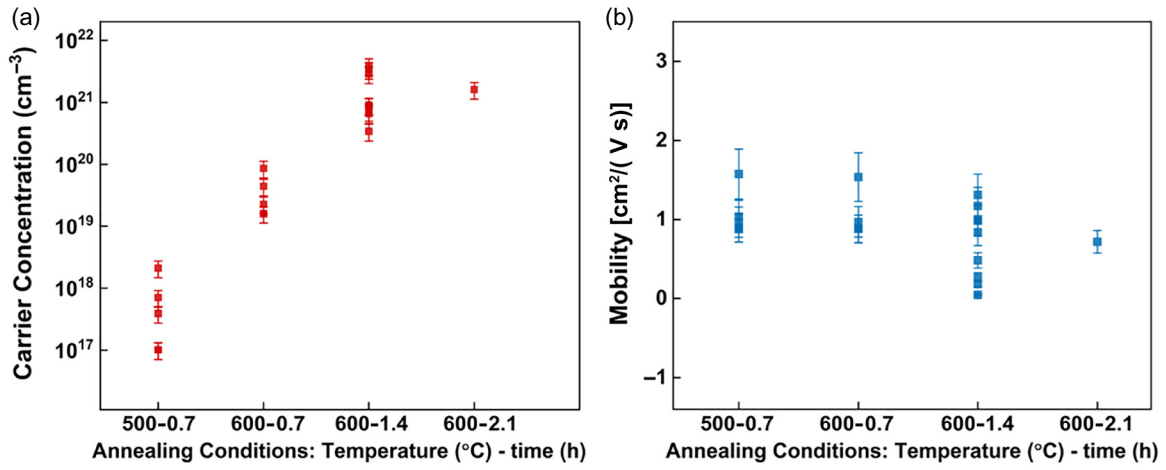


FIG. 3. The room-temperature electrical properties of annealed BaZrS₃ thin films: (a) the carrier concentration and (b) the carrier mobility. The vertical error bars reflect the uncertainty in the thickness measurements and the instrument error.

visibly darker, as seen in the optical images (see Fig. S2 in the Supplemental Material [27]). The 600-1.4 sample shows a carrier concentration in the metallic regime, which also correlates with the high absorption in all wavelength ranges (Fig. 2). The results from the Seebeck and Hall measurements are correlated by calculating the effective mass of the electrons [38]. The effective mass is found to be increasing with the annealing temperature and duration, with $0.2m_o$ – $0.6m_o$ for the 500-0.7 and 600-1.4 samples (where m_o is the electron rest mass). These values match with those calculated using density-functional theory (DFT) studies in the literature [23,24,39].

Figure 3(b) presents the charge-carrier mobility of films annealed under different conditions. The figure shows that the carrier mobility of the annealed BaZrS₃ films did not exhibit any significant dependence on the annealing conditions and that the values remained around $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, with only slight deviations. While there may be some

influence of annealing on carrier mobility, the small values and minimal variations hinder further analysis. Given that the carrier mobility remains unchanged despite the carrier concentration increasing by orders of magnitude, it can be suggested that ionized-impurity scattering does not dominate charge transport at room temperature in these films.

Temperature-dependent Hall measurements were further employed to investigate the dominant scattering mechanism and characteristics of the charged defects in BaZrS₃ thin films. In Fig. 4(a), we show the semilogarithmic plot of the mobility ($\log \mu$) versus the temperature of sample 600-0.7 in the range of 10–300 K. The blue spheres represent experimental data. The electron mobility first increases with the temperature in the range of 10–125 K and then monotonically decreases at high temperatures ($>125 \text{ K}$). This shows the dominance of ionized-impurity scattering for the former and of the

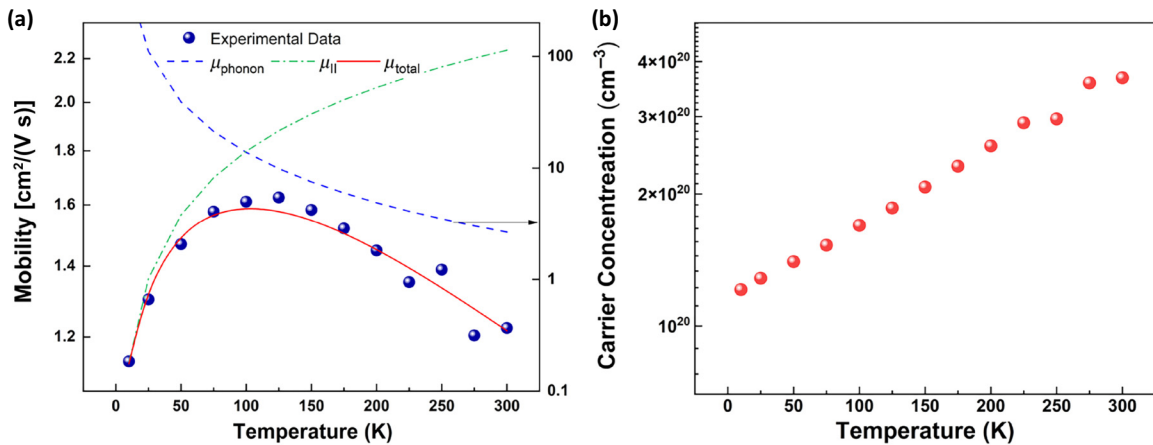


FIG. 4. A semilogarithmic plot of (a) the temperature-dependent mobility and (b) the carrier concentration of sample 600-0.7 in the range of 10–300 K.

phonon scattering mechanism for the latter. The experimental data are modeled by calculating the mobility using the ionized-impurity scattering ($\mu_{\text{II}} \propto T^{3/2}$) and phonon-assisted-scattering ($\mu_{\text{phonon}} \propto T^{-3/2}$) mechanisms and are represented with dashed-dotted green and dashed blue lines, respectively [40–42]. The solid red line is the effective mobility (μ_{total}), calculated by Matthiessen's rule ($1/\mu_{\text{total}} = 1/\mu_{\text{II}} + 1/\mu_{\text{phonon}}$) [41,43]. The fitting of the data shows that the low temperature range is dominated by ionized-impurity scattering; however, the dependence does not follow $T^{3/2}$ but $T^{0.2}$. The reason is the high carrier concentration present even at low temperatures [Fig. 4(b)], which dominates the screening, and that the dependence on the temperature becomes less significant [42]. The mobility decreases with the temperature at $T > 125$ K and can be modeled with a phonon-scattering mechanism. This indicates that the room-temperature mobility is dominated by the phonon-scattering mechanism. The dominance of phonon scattering in BaZrS₃ has also been discussed in recent first-principles calculations by Yuan *et al.* [24]. The experimental mobility values are lower than the calculated values, which is due to the polycrystalline nature of the films and the presence of defects. The scattering from grain boundaries and impurities negatively affect the mobility. However, as the room-temperature mobility is dominated by phonon scattering, it is difficult to achieve very high carrier mobility in BaZrS₃ thin films. The dominance of phonon scattering at room temperature further supports the fact that the room-temperature mobility does not vary significantly after vacuum annealing [Fig. 3(b)]. Even though there are higher number of ionized-impurity centers in annealed samples, the mobility remains almost unchanged.

In Fig. 4(b), we show the carrier concentration of sample 600-0.7, measured between 10 K and 300 K. The carrier concentration increases with temperature, which is a typical semiconductor behavior [43–45]. However, the carrier concentration remains within a narrow range (1×10^{20} to 4×10^{20} cm⁻³) and even at 10 K the value is as high as 1×10^{20} cm⁻³. This indicates that defects are ionized to a high degree, even at low temperatures. With such a high defect concentration, the wave functions of these defects overlap and they can no longer be considered discrete localized levels within the band gap [44,46,47]. Instead, they form an impurity band. Impurity metallic behavior is an extreme example of this, where the impurity band becomes contiguous with one of the principal bands. In the present case, this behavior is not so extreme, as evidenced by the nonconstant monotonically increasing carrier concentration between 10 K and 300 K [Fig. 3(c)] [44]. Using the Arrhenius equation at high temperatures, a thermal activation energy of approximately 8 meV was determined, suggesting that the donor defect behaves like a weak-impurity-metal state. In this case, the impurity band consists of defect states close to the conduction-band minimum (CBM) [44]. This shallow-defect nature

of the S vacancy in BaZrS₃ is also predicted by hybrid-functional defect calculations [21,24]. These calculations show that V_S defects have a low formation energy under S-poor conditions, aligning with the high defect concentration observed in the films after annealing, which reaches up to 10^{21} cm⁻³. Similar defect studies in silicon and germanium demonstrate that the activation energy decreases with increasing defect density and eventually approaches zero when the impurity band merges with the CB or VB [46,47]. The shallow nature of S-vacancy defects and the high number density further suggest that it is difficult to achieve *p*-type BaZrS₃. Although there are shallow-acceptor defects, there is a high possibility of their compensation by S vacancies. This is very similar to intrinsically doped *p*-type Cu₂O, where the low formation energy of Cu-vacancy defects makes it difficult to obtain *n*-type Cu₂O [43,48–50]. Yuan *et al.* have also discussed the compensation of shallow-acceptor defects (Zr-*V*, Ba-*V*, and Ba_{Zr}) by V_S donors in their first-principles calculations [24].

The combined results from our optical and electrical measurements indicate that annealing BaZrS₃ thin films creates defects and that their number density increases with an increasing annealing temperature and/or duration. These defects are most likely S vacancies, given that the samples are annealed in an S-deficient atmosphere and that sulfur has a significant vapor pressure, unlike the other elemental constituents of the material. Also, the temperature-dependent carrier concentration indicates a low activation energy of the defect. This is consistent with existing theoretical studies on BaZrS₃, which indicate that the positive ionization-energy level associated with S-vacancy defects lies close to the CBM [21–24]. The presence of this impurity band near the CBM likely contributes to the red shift in the absorption edge (Fig. 2). This behavior is closely analogous to that of oxide perovskites treated under O-deficient conditions [36,37]. To further substantiate this hypothesis, chemical composition analysis was conducted before and after annealing, which will be discussed in the next section.

D. Chemical composition

In Fig. 5, we compare the atomic percentage of sulfur in both as-prepared and annealed BaZrS₃ films using surface EDS, which measures the composition from the top of the sample, providing data that are more sensitive to the surface. To ensure data reliability, different locations on the sample were measured, as shown in Fig. 5. While we cannot rely on EDS to quantify the absolute S content (which should be 60 at% in stoichiometric BaZrS₃), the relative change due to postannealing shows a clear trend, with a drop of around 2% for the most extreme postanneal conditions.

Considering the density of BaZrS₃ to be 4.22 g/cm³, a volume of 1 cm³ corresponds to 7.8×10^{21} formula units [11], which translates to 2.3×10^{22} S atoms per cm³.

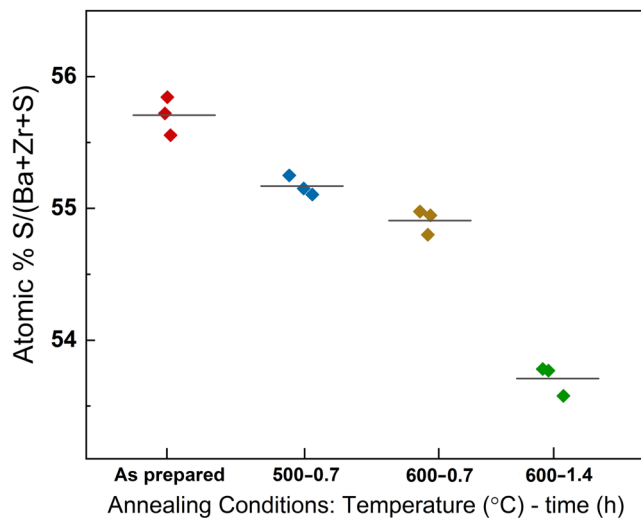


FIG. 5. The chemical composition of both as-prepared and annealed BaZrS₃ films, measured via EDS. Different data points on the *Y* axis for the same sample (*X* axis) represent values measured at different locations on the sample and the horizontal line indicates the median.

Based on this, a reduction of S by 2% leads to an electron concentration of almost $1 \times 10^{21} \text{ cm}^{-3}$ (see the calculation in the Supplementary Material [27]). Here, the assumption is that all S-vacancy defects are completely ionized ($V_S^{\bullet\bullet}$), with each defect donating two electrons to the CB. These calculated values closely match the values observed in Hall measurement, as shown in Fig. 3(a). Although the difference in the S percentage correlates well with the electrical data, it is important to acknowledge the difficulty in measuring an overall change of 1–2% in S content accurately. This is especially true given the potential for a concentration gradient with depth (most S loss is expected from the surface) and the fact that some S loss could be compensated by oxygen inclusion. For further validation, TOF ERDA was conducted on these samples, providing more precise values of chemical composition along the depth. The as-prepared BaZrS₃ sample had a composition of 19.1% Ba, 21.5% Zr, and 59.4% S, indicating a nearly stoichiometric composition in the film. The depth profiles of as-prepared and annealed samples of Ba, Zr, and S are shown in Fig. S5 in the Supplementary Material [27]. One observation is that the bulk composition of the as-prepared sample closely matches that of the annealed samples, indicating that the BaZrS₃ phase remains intact. However, no significant reduction in sulfur percentage was observed. This may be due to the low deviation expected from annealing compared to the error bars of the measurement. A significant sulfur reduction was observed at the surface of the 500-0.7 sample, which was mostly compensated by oxygen. The reason for this is unclear and may be related to a sample anomaly. There was no pattern in oxygen inclusion that might have otherwise suggested a role

of oxidation in the formation of defects in the BaZrS₃. In conclusion, composition measurements alone cannot conclusively prove the existence of V_S . Nevertheless, given the overall picture, the creation of V_S is considered the most consistent explanation for the observations, particularly the induction of *n*-type defects via vacuum annealing.

E. XPS analysis

The chemical compositions of the BaZrS₃ surfaces were further investigated using XPS at two different energies: a more surface-sensitive Al K α (1.487 keV) and Ga K α (9.25 keV), where the information depth reaches tens of nanometers. The survey scans acquired at both energies (Al K α and Ga K α) all reveal characteristic core levels of the constituent atoms Ba, Zr, and S of the BaZrS₃ compound (see Figs. S6 and S8 in the Supplemental Material [27]), with additional contributions from Sn, O, and C. These signatures are related to surface impurities formed during material synthesis and surface oxidation upon subsequent exposure to air. The surveys for samples 600-0.7 and 600-1.4 detect an unknown impurity species at an approximately 305-eV binding energy (see Fig. S6 in the Supplemental Material [27]), probably coming from the annealing furnace. The absence of this impurity peak in the Ga K α survey for all the samples establishes that these impurities must be confined within the first few nanometers of the surface and is unlikely to affect the bulk properties of the films.

The annealing process also affects chemical bonding of S atoms in the films. The Al K α XPS measurements (see Figs. S6 and S7 in the Supplemental Material [27]) reveal peaks corresponding to oxidized S species, except for sample 600-1.4, where these contributions disappear in favor of the lowest-binding-energy S peak (see Fig. S7 in the Supplemental Material [27]), identified previously as the S peak of BaZrS₃ [8,51]. This deviation from other samples is likely due to the presence of the observable impurity, which protects sulfur from oxidation after annealing, not the annealing process itself. The measurements using Ga K α , on the other hand, detect mainly the perovskite S peak, significantly lower O content, and no adventitious C 1s peak (see Fig. S8 in the Supplemental Material [27]). Moreover, for Ga K α , the peaks related to Sn, visible for the as-prepared and 500-0.7 samples, disappeared as the annealing temperature increased to 600 °C, similar to the observation from Al K α . All these observations indicate that the annealing process affects the surface chemistry at up to at least 10 nm from the surface, while the bulk of the films is primarily comprised of the BaZrS₃ perovskite. Nonetheless, XPS analysis concludes that the annealing process in vacuum has the additional advantage of improving surface quality, along with enhancing electrical properties.

F. Band diagram

The VB spectra acquired with Ga K α were utilized to determine the energy shift of the VBM with respect to the Fermi level (see Sec. II). In Fig. 6, we compare the VB spectra of the as-prepared and annealed BaZrS₃ thin films. It is found that upon annealing, the VB-edge position shifts toward higher binding-energy values with respect to the Fermi level. For the as-prepared sample, the VBM appears at 0.7 eV versus the Fermi level, consistent with findings from previous work [51]. As for the VB spectra, a similar offset trend is observable for the position of the S 1s peaks for the different samples (see Fig. S9 in the Supplemental Material [27]). From the fit of the S 1s peaks for the samples, the amount of shift of the VBM between the samples was determined more precisely. The as-prepared sample shows the main S 1s peak position at 2468.7 eV. When the samples are annealed at 500-0.7 and 600-0.7, the main S 1s peak position appears at 2469.2 eV. Finally, the sample annealed at 600-1.4 has a S 1s main peak at 2469.5 eV, with an increase in the binding energy of 0.7 eV compared to the as-prepared sample. Considering the band-gap values extracted from ultraviolet-visible (UV-Vis) measurements (Fig. 2), the CBM position can be identified, which allows us to compile the band diagram for all samples in Fig. 7 [1,15,52].

From the figure, one can conclude that annealing induces the formation of donor defects, thereby shifting the Fermi level toward the CB in BaZrS₃ thin films. Analysis of the VBM reveals how the annealing temperature and annealing time can be utilized as critical parameters to control the transport properties of BaZrS₃ thin films.

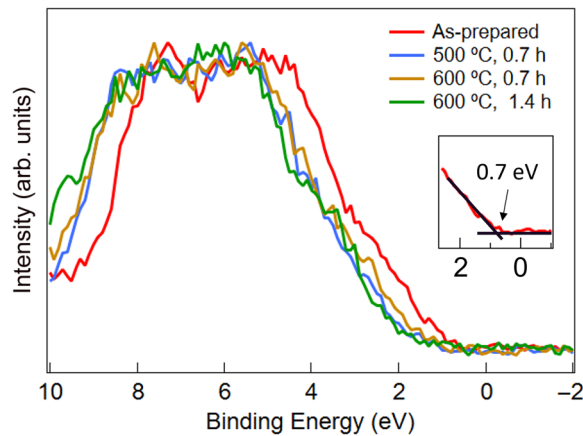


FIG. 6. The valence bands (VBs) of both as-prepared (green) and annealed BaZrS₃ films, measured via x-ray photoelectron spectroscopy with photon energy 9.25 keV. The spectra are energy calibrated by setting Au 4f_{7/2} at 84.0 eV. The intensity is normalized for ease of comparison. The inset shows an enlargement of the VB edge of the as-prepared sample for determination of the valence-band maximum (VBM).

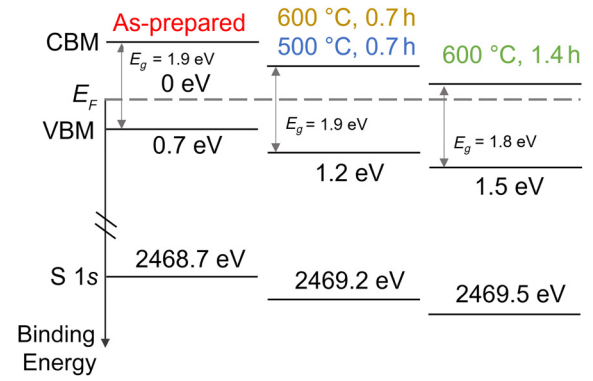


FIG. 7. The energy diagram of the BaZrS₃ samples—as prepared, 500-0.7, 600-0.7, and 600-1.4—as derived from XPS analysis and combined with UV-Vis measurements. The binding-energy scale starts from the Fermi level at 0 eV, as from the spectroscopy measurements calibrated versus Au 4f_{7/2}.

The position of the Fermi level above the midgap region in annealed samples corroborates the observed *n*-type conductivity in both the Hall and the Seebeck-coefficient results. The shift of the Fermi level toward the CBM, as depicted in Fig. 7, aligns with the findings from the Hall measurements. As the annealing temperature and duration increase, as shown in Fig. 3(a), the carrier concentration rises, causing the Fermi level to shift further toward the CBM in Fig. 7. Note that the Fermi level of the as-prepared sample lies below the midgap region ($E_g/2$), suggesting a near-intrinsic nature. The extremely high resistivity of the as-prepared films hindered precise electrical measurements, preventing definitive conclusions about the defects. The high resistivity could be due to low hole mobility in BaZrS₃ or the low defect density of acceptor defects [24]. Based on the synthesis conditions, subsequent compositional analysis, and theoretical studies, it is believed that the dominant acceptor defects are likely Ba-*V* and/or S_i [21–23]. However, a systematic study is required to further confirm these assertions. Given the hypothesis regarding a dopant-induced impurity band, accurately determining the Fermi-level position through electrical data and indirect comparison with XPS values presents a challenge. However, there is qualitative agreement between the XPS findings and the electrical data, linking structural analysis with functional properties.

IV. SUMMARY

To summarize, the effect of annealing BaZrS₃ thin films in an S-poor atmosphere and its impact on charge-transport properties were investigated. Vacuum annealing ($<1 \times 10^{-6}$ mbar) is expected to reduce the band gap and induce what are likely to be S-vacancy (*V_S*) defects. Consequently, the otherwise insulating BaZrS₃ films exhibit *n*-type conductivity after vacuum annealing, with a significant increase of up to 100 S/cm. Notably,

the number density of V_S defects demonstrates a direct correlation with the annealing temperature and duration. It increases from the order of 10^{17} to 10^{21} cm⁻³ with an annealing temperature going from 500 to 600 °C and a duration from 0.7 to 1.4 h. The carrier mobility in films remains modest (approximately 1 cm² V⁻¹ s⁻¹). Further optimization of the synthesis process, such as increasing the grain size in the thin films, is necessary to improve the carrier mobility. S-vacancy defects with a low activation energy of 8 meV and a high carrier density (in the order of 10^{21} cm⁻³), even at 10 K, are expected to be shallow-donor defects and to form an impurity band close to the CBM. This study clarifies that ionized impurities play only a secondary role in affecting room-temperature mobility and that phonon scattering governs the charge transport at temperatures above 125 K. Compositional analysis via EDS shows that the S atomic percentage is reduced by more than 2% upon annealing, resulting in a charge carrier concentration of approximately 1×10^{21} cm⁻³ at room temperature, in agreement with the Hall measurements. The emergence of an n type of conductivity post annealing is also evident from the XPS results, where the Fermi level, initially positioned around the midgap ($E_g/2$) region in as-prepared film, starts to shift toward the CBM with an increasing annealing temperature and duration. The findings of this study reveal a useful possibility to control the conductivity over a large range by subjecting BaZrS₃ to an S-poor atmosphere.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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