Realization of BaZrS$_3$ chalcogenide perovskite thin films for optoelectronics

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Abstract

BaZrS$_3$ is a prototypical chalcogenide perovskite, an emerging class of unconventional semiconductor. Recent results on powder samples reveal that it is a material with a direct band gap of 1.7-1.8 eV, a very strong light-matter interaction, and a high chemical stability. Due to the lack of quality thin films, however, many fundamental properties of chalcogenide perovskites remain unknown, hindering their applications in optoelectronics. Here we report the fabrication of BaZrS$_3$ thin films, by sulfurization of oxide films deposited by pulsed laser deposition. We show that these films are n-type with carrier densities in the range of $10^{19}$-$10^{20}$ cm$^{-3}$. Depending on the processing temperature, the Hall mobility ranges from 2.1 to 13.7 cm$^2$/Vs. The absorption coefficient is $> 10^5$ cm$^{-1}$ at photon energy $> 1.97$ eV. Temperature dependent conductivity measurements suggest shallow donor levels. By assuring that BaZrS$_3$ is a promising candidate, these results potentially unleash the family of chalcogenide perovskites for optoelectronics such as photodetectors, photovoltaics, and light emitting diodes.

**KEYWORDS:** chalcogenide perovskite, absorption coefficient, Hall effect, carrier mobility, defects
Introduction

Semiconductors can be considered as the backbone of modern society. They have found broad applications in computer chips, power electronics, optical sensors, light emitting diodes (LEDs), solid-state lasers, and solar cells. Most conventional semiconductors are covalent materials with four-fold coordination of both the cations and anions. During last decade, however, the organic-inorganic halide perovskites have attracted considerable attention, as they rival the conventional semiconductors for photovoltaics in an unprecedented way [1-8]. These are ionic materials, which are characterized by a higher coordination maximizing the Coulomb attraction between cations and anions. The strong ionicity is believed to minimize the possibility of forming deep level anti-site defects responsible for non-radiative carrier recombination. Compared to conventional semiconductors, the halide perovskites have unusually low carrier concentration (~10^{13}/cm^3) and extremely long carrier lifetime (on the order of 1 µs) [9]. The power conversion efficiency of solar cells made of halide perovskites has witnessed a stellar rate of increase, from an initial PCE of 3.8% in 2009 [10] to above 25% in 2019 [11].

Specifically, perovskites refer to a class of crystalline compounds adopting the generic chemical formula ABX₃, where cation “B” has six nearest-neighbor anions. “X” and cation “A” sits in a cavity formed by eight corner-shared BX₆ octahedra. They demonstrate a rich spectrum of physical phenomena from 2D electron gas, ferroelectricity/piezoelectricity, ferromagnetism, colossal magnetoresistance, multiferroicity, ionic conductivity, to superconductivity [12-17]. The most commonly studied perovskites are the complex metal-oxides, where X is oxygen. Due to their multifunctionality and highly tunable physical properties, the oxides are an extremely important class of materials for technological applications.
Over the spectrum of covalency and iconicity, conventional semiconductors and oxide/halide perovskites are two extremes. Covalent bonding is directional, making the electronic and optical properties sensitive to bond distortions. In contrast, ionic bonding is often associated with a strong electron correlation, as the dielectric screening is reduced by the loss of shared valence electrons. Balancing ionicity with covalency therefore provides opportunities for discovering semiconductors with properties and performances unattainable in conventional semiconductors. In this regard, it is quite surprising that only limited effort has been devoted to the development of materials intermediate between covalency and ionicity.

Recently, chalcogenide perovskites have emerged as a novel class of semiconductor, where the anions are S and Se instead of O. They are more ionic than the conventional semiconductors but less so than either oxides or halides. Despite being synthesized more than a half century ago, these compounds have received little attention [18-22]. As a result, there is limited knowledge of their physical properties [23, 24]. The situation changed only recently, after we theoretically screened [25] 18 ABX$_3$ chalcogenide materials, predicting exciting semiconductor properties for photovoltaics. For example, several of them were found to be direct bandgap semiconductors combining both a strong light absorption and a good carrier mobility, which is a rare trait for semiconductors and are hence particularly attractive for optoelectronic applications. Subsequent experimental efforts have succeeded in synthesizing several of the prototypical chalcogenide perovskites as well as related phases including BaZrS$_3$, CaZrS$_3$, SrTiS$_3$, SrZrS$_3$[26], and SrHfS$_3$ [27, 28]. In particular, we further confirmed that BaZrS$_3$ possesses a distorted perovskite structure with a ~1.7 eV [27] bandgap and strong light absorption, in good agreement with our theory. The material was found to be exceptionally stable against pressure [29], moisture and oxidation [27].
The structural and physical properties show little degradation four years after the synthesis (see Fig. S1 in the Supporting Information, SI)

Besides, Niu et al. [26] synthesized and characterized BaZrS$_3$ and SrZrS$_3$. The latter has two different phases, with $\beta$-SrZrS$_3$ showing a bandgap of 2.13 eV and green light emission. They further demonstrated a giant optical anisotropy in hexagonal BaTiS$_3$ crystal [30]. Meng et al. [31] studied the BaZr$_{1-x}$Ti$_x$S$_3$ alloy system, suggesting a limited concentration range before phase separation takes place. Optical and thermoelectric properties of SrHfSe$_3$ and Sr$_{1-x}$Sb$_x$HfSe$_3$ were also studied [32]. Intense green luminescence characteristics were found in both undoped and heavily n- and p-doped SrHfS$_3$ [28]. On the theory front, Ruddlesden–Popper perovskite sulfides A$_3$B$_2$S$_7$ were proposed as a new family of ferroelectric photovoltaic materials in the visible [33]. Using machine learning, Agiorgousis et al. isolated Ba$_2$AlNbS$_6$, Ba$_2$GaNbS$_6$, Ca$_2$GaNbS$_6$, Sr$_2$InNbS$_6$, and Ba$_2$SnHfS$_6$, out of 450 chalcogenide double perovskites, as the most promising photovoltaic materials [34]. Guided by computational screening of ternary sulfides, Kuhar et al. also identified and synthesized LaYS$_3$ with a strong light absorption and photoluminescence as a promising candidate for photoelectrochemical water splitting [35].

While these studies reveal that chalcogenide perovskite and related compounds are indeed a unique family of optoelectronic materials with promises, a number of fundamental material properties such as the carrier type, concentration and mobility, optical absorption coefficient, and defect properties remain largely unexplored. This is due in large part to the lack of thin film samples, as most experiments have focused on powder or single crystal bulk samples. Lack of the thin film samples thus not only limits our basic understanding, but also becomes an obstacle against device applications.
In this paper, we report the first fabrication of BaZrS\textsubscript{3} thin films, by sulfurization of BaZrO\textsubscript{3} precursor films deposited by pulsed laser deposition. We show that films fabricated by this method are n-type with carrier density in the range of 10\textsuperscript{19}-10\textsuperscript{20} cm\textsuperscript{-3}. The Hall mobility ranges from 2.1 to 13.7 cm\textsuperscript{2}/Vs depending on processing temperature. The optical absorption coefficient is greater than 10\textsuperscript{5} cm\textsuperscript{-1} at photon energy greater than 1.97 eV. Temperature dependent conductivity measurements suggest shallow donor levels. Although further optimization is needed, our present results suggest that BaZrS\textsubscript{3} thin films are promising for optoelectronic applications.

**Experimental**

**Synthesis of BaZrS\textsubscript{3} thin films**

BaZrO\textsubscript{3} thin films with 100 nm thickness were deposited on sapphire substrates via a PLD-450 Pulsed Laser Deposition (PLD) system at 800\textdegree}C. Oxygen partial pressure of 2.0 Pa was introduced into the deposition chamber with a background vacuum level higher than 10\textsuperscript{-5} Pa. The laser frequency and energy was set to be 5 Hz and 250 mJ, respectively. The as-deposited BaZrO\textsubscript{3} films were then loaded into a 2" quartz tube furnace for sulfurization. The sulfurization procedure lasted for 4 hours in an H\textsubscript{2}/N\textsubscript{2} atmosphere at 900, 950, 1000, and 1050 \textdegree}C, respectively. Sulfurization was also done at 1050 \textdegree}C for 2 hours for the samples used for photodetector measurements. CS\textsubscript{2} was introduced at 800\textdegree}C as the sulfur source, through H\textsubscript{2}/N\textsubscript{2} gas bubbling at a flow rate of 20-25 standard cubic centimeters per minute (sccm).

A Rigaku Ultima IV X-ray diffraction (XRD) system with an operational X-ray tube power of 1.76 kW (40 kV, 44 mA) and Cu target source was used to acquire the X-ray diffraction pattern (XRD) for investigating the crystal structure. The XRD measurements were performed under theta/2 theta scanning mode and continuous scanning type with a step size of 0.02\textdegree}. A Renishaw
inVia Raman Microscope was used to measure the room temperature Raman and Photoluminescence (PL) spectra with a 1200 l/mm grating, 50× objective lens, and 514 nm laser. Time resolved PL (TRPL) on the BaZrS$_3$ film was done using an amplified ultrafast excitation laser (repetition rate 250 kHz) with a pulse duration of <200 fs and a wavelength of 400 nm. TRPL was collected with a microscope objective with an NA of 0.2 and spectrally and temporally detected on a Hamamatsu streak camera with a time-resolution of 32 ps. A Labsphere RSA-HP-8453 reflectance spectroscopy accessory attached to Agilent 8453 ultra-violet/visible (UV-vis) spectroscopy system was used to obtain the absorption spectrum. Surface morphology and energy-dispersive X-ray elemental analysis was performed using a Focused Ion Beam-Scanning Electron Microscope (FIB-SEM) – Carl Zeiss AURIGA CrossBeam with an Oxford EDS system.

**Atomic resolution imaging**

Atomically resolved high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) images were acquired on a FEI Titan Themis Cube with an X-FEG electron gun and a DCOR aberration corrector operating at 300 kV. The semi convergence angle used was 30.1 mrad. The inner and outer collection angles for the STEM images ($\beta_1$ and $\beta_2$) were 54 and 143 mrad, respectively. The beam current was about 20 pA for the ADF imaging. All imagings were performed at room temperature. The EDX elemental mapping was acquired using the SuperEDX system equipped with four detector configurations.

**Device fabrication and optical and transport measurements.**

A two-terminal device was fabricated for photodetector measurements. Au electrodes were deposited using an e-beam evaporator through a mask with a thickness of 50 nm and a gap of 100
μm between the electrodes. A Keithley 2425 source/meter was used as a voltage source and a Keithley 6485 picoammeter was used as the current meter for I-V measurements under dark and illumination conditions. The illumination was provided by a diode laser at a wavelength of 532 nm with a power of 46 mW and spot size of 5 mm. For Hall effect measurements, the sample was cut into a Hall bar with dimension of 6 mm×1 mm, and directly wired using silver paste. The transport data were acquired using a Quantum Design Physical Property Measurement System (PPMS) interfaced to a Keithley 2425 source/meter and two Keithley 2182 voltmeters. The schematic drawing of the devices are shown in Figure S2 of the Supporting Information.

**Results and discussion**

**Structural characterizations:** The XRD pattern of a BaZrS$_3$ thin film sulfurized at 1050 °C is shown in Figure 1(a). It can be seen that the film is polycrystalline with no preferential orientation. The peaks can be matched to those of the standard file JCPDS 00-015-0327, showing that the sample possesses an orthorhombic distorted perovskite structure with Pnma space group. The extremely intense peak is the (0001) peak from the sapphire substrate. In Figure 1(b), the Raman spectrum of the BaZrS$_3$ film measured at room temperature is shown. Five broad peaks can be observed between 50-400 cm$^{-1}$, which are identified as $B_{1g}^1$, $A_g^4$, $B_{2g}^6$, $B_{1g}^4$, and $B_{1g}^5$ modes. The peak positions match with the theoretical predictions [27, 29] and published experimental reports [26, 27]. Figures 2(a) -2(d) show the SEM images of BaZrS$_3$ thin films sulfurized from 900 °C to 1050 °C for 4 hours, respectively. It can be seen clearly that the films are polycrystalline, with the grain sizes increasing with increasing sulfurization temperature. As shown in Fig. 2(e), the grain size increases from 0.43 ± 0.01 μm at 900 °C to 1.19 ± 0.06 μm at 1050 °C. Such grain sizes are in the optimal range for certain optoelectronic applications such as photovoltaics. A typical EDX
spectrum of the BaZrS$_3$ film synthesized at 1050 °C is shown in Figure 2(f). The atomic ratio of Ba: Zr: S is found to be 1: 1.17: 2.91, close to the stoichiometric composition. The sulfur concentration ranges from 56.9 to 57.8% at 6 different locations measured on the same film, suggesting a small inhomogeneity accompanied by a slight sulfur deficiency (Table S1 in Supporting Information). The sulfur deficiency is likely caused by sulfur vacancies [27], due to the high processing temperature. We notice that this is analogous to oxygen vacancies commonly observed in oxide perovskites [36-39]. At lower sulfurization temperatures, the S:Ba composition ratio decreases, as shown in Fig. S5 in SI. However, this should not be interpreted as increasing sulfur vacancies, but instead incomplete conversion of BaZrO$_3$ [19]. Further investigations using aberration-corrected scanning transmission electron microscope (STEM) are shown in Fig. 2(g-i).

The atomically resolved high-angle annular dark field (HAADF) image in Fig. 2(g) reveals a well-crystallized structure much resembles ABO$_3$ perovskites, consistent with the orthorhombic perovskite phase observed in the XRD measurements. Meanwhile, individual S, Zr, and Ba atomic column signals are clearly identified by the atom-by-atom EDX elemental mapping in another region of the crystal view along a different zone axis (Fig.2(h)) , as shown in Fig. 2(i). These atomic resolution characterizations indicate that each grain maintains well crystalline structures, demonstrating the high quality of the as-synthesized BaZrS$_3$ polycrystalline thin film.

**Optical characterizations:**

The band gaps of BaZrS$_3$ with distorted perovskite structure have been theoretically calculated to be around 1.7-1.85 eV [25, 27, 31, 40-41] and experimentally verified to be within the same range [26, 27, 31]. In Figure 3(a), the UV-Vis absorption spectrum as a function of photon energy is plotted for the BaZrS$_3$ thin film synthesized at 1050 °C. The thin film geometry allows the extraction of the absorption coefficient $\alpha$. It can be seen that $\alpha$ rises rapidly in the range of 1.7-1.8
eV, and exceeds $10^5$ cm$^{-1}$ at photon energy $>1.97$ eV. This confirms the strong light absorption of the BaZrS$_3$. The band gap energy can be estimated from the Tauc plot in Fig. 3(b). The value is found to be 1.82 eV, slightly higher than our previously reported value for powder samples. The PL spectrum shows a broad peak centered at 1.81 eV, with a width of ~ 200 meV, in good agreement with the absorption measurement. The time resolved PL is shown in Fig. 3(c). A bi-exponential fitting [42, 43] is found to accurately describes the data. Two time constants extracted are $\tau_1=40$ ns and $\tau_2=400$ ns, which suggest that the sample may be inhomogeneous, e.g., photocarrier separation at domain boundaries could account for the slower recombination with a longer $\tau$.

**Transport measurements**

To quantify the characteristics of carrier transport, Hall measurements were performed on the four samples with sulfurization temperatures ranging from 900 to 1050 °C. All samples showed n-type conductivity, suggesting that the dominant carriers are electrons. This is likely due to the sulfur vacancies, as each of them will contribute to 2 excess electrons. The carrier density obtained from the Hall effect measurements ranges from $1.06\times10^{19}$ to $4.7\times10^{20}$ cm$^{-3}$, as shown in Fig 4(a), suggesting substantially high doping levels. The conductivity is in the range of 3.52 to 588 S/cm. Combing these results, the Hall mobility can be calculated and plotted as a function of sulfurization temperature in Fig. 4(c). It can be seen that the Hall mobility increases monotonically with increasing sulfurization temperature. This is expected as higher processing temperature leads to larger grain size and higher crystallinity, both suppresses carrier scattering. The mobility at 1050 °C is found to be 13.7 cm$^2$/Vs. This value is comparable to that of halide perovskites, such as MAPbI$_3$ [44]. The limiting factor seems to be the carrier concentration. We expect that with proper passivation and reduction of carrier density, this value can be improved by an order of magnitude.
Conductivity was measured as a function of temperature to elucidate the origin of the carriers. It can be seen that the conductivity increases with increasing temperature. Although the limited temperature and conductivity range makes differentiating transport mechanisms difficult, the conductivity vs. temperature can be best fitted by the Efros-Shklovskii variable range hopping model, where $G = G_0 \exp \left( -\frac{E}{k_B T} \right)$ [45]. On the other hand, a fitting using Arrhenius Law shows a slightly larger deviation from experimental data (Fig. S7 in SI). An activation energy is extracted to be 1.7 meV. This behavior may be understood as related to the average ionization energy of the donor levels to the conduction band edge, assuming a narrow distribution of density of states for such levels resulting from sulfur vacancies. Our results suggest that sulfur vacancies act as shallow defect levels that are readily ionized at room temperature. Further systematic studies are needed to identify and quantify the defects in BaZrS$_3$ thin films, and pinpoint the carrier transport mechanisms.

**Photodetector measurements**

To investigate the suitability of the BaZrS$_3$ films for optoelectronic applications, photodetector devices were fabricated using the samples sulfurized at 1050 °C. The I-V curves in the dark and under illumination are plotted in Fig. 5. For the sample sulfurized at 1050 °C for 4 hrs, the difference between the I-V curves in the dark and under illumination is small, due to the large carrier concentration of $2.7 \times 10^{20}$ cm$^{-3}$ (Fig. 5(a)). Postulating that prolonged high temperature processing leads to sulfur vacancy formation, increasing the carrier concentration, we reduced the sulfurization time in an attempt to enhance the photo-response. As can be seen from Fig. 5(b), reducing the sulfurization time to 2 hrs significantly increases the sample resistivity and decreases the dark current by three orders of magnitude, suggesting that carrier density due to
sulfur vacancy is greatly reduced. We are not able to perform Hall effect measurement to determine the carrier concentration on this sample due to its high resistance. Nevertheless, as seen in Fig. 5(b), the photo-response is significantly enhanced, with an ON/OFF ratio of 20 at the bias voltage of 2 V. These results indicate that for better photodetector performance, it is crucial to suppress the dark current by further reducing the carrier concentration. We suggest that p-type doping (e.g. by Y or La) or sulfurization at high pressure can be considered to passivate the sulfur vacancy states.

Conclusion

In conclusion, we have fabricated BaZrS₃ chalcogenide perovskite thin films using sulfurization of oxide films deposited by PLD. The films show exceptionally strong light absorption with an absorption coefficient > 10⁵ cm⁻¹ at photon energy > 2 eV. The films are n-type with good carrier mobility of ~ 13.7 cm²/Vs. The films are defect tolerant with shallow donors possibly originating from sulfur vacancies. Combined with its earth abundancy, high stability and non-toxicity, BaZrS₃ is a promising candidate for optoelectronics such as photodetectors, photovoltaics and light emitting diodes. As importantly, the findings here open the door for fabricating other high quality chalcogenide perovskite thin films for both fundamental studies and device applications.

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**Figure captions**

Figure 1. (a) An X-ray diffraction pattern of a BaZrS$_3$ film sulfurized at 1050°C. The extremely intense peak comes from the (0001) peak of the sapphire substrate; (b) A Raman spectrum of the BaZrS$_3$ film measured at 300K.

Figures 2. (a)-(d) Typical SEM images of BaZrS$_3$ thin films sulfurized at temperatures of (a) 900, (b) 950, (c) 1000 and (d) 1050 °C, respectively. (e) The measured average grain size as a function of sulfurization temperature for BaZrS$_3$ thin films, obtained from corresponding SEM images. (f) An EDX spectrum of the BaZrS$_3$ film sulfurized at 1050 °C. The atomic ratio of Ba: Zr: S is found to be 1: 1.17: 2.91. Inset is an SEM image of the EDX measurement area. (g) Atomically resolved HAADF image of a BaZrS$_3$ thin film sulfurized at 900 °C. Inset is the Fast Fourier Transformation (FFT) of the image. (h) Atomically resolved HAADF image of another region of the sample viewed in a different zone axis. (i) EDX atom-by-atom elemental mapping corresponding to the center part of the area shown in (h).

Figure 3. (a) The UV-vis absorption spectrum; (b) Red curve: the Tauc plot derived from the absorption spectrum; Black curve: the PL spectrum; (c) Time resolved PL spectrum of the BaZrS$_3$ thin film sulfurized at 1050 °C for 4 hrs. Time constants $\tau_1$ and $\tau_2$ are found to be 40 ns and 400 ns, respectively from the bi-exponential fitting.

Figure 4. (a) Carrier density, (b) conductivity, and (c) Hall mobility of BaZrS$_3$ thin films as a function of sulfurization temperature for samples sulfurized for 4 hrs, obtained from the Hall effect measurements. (d) Conductivity plotted in logarithmic scale as a function of $T^{-1/2}$ for the BaZrS$_3$ film sulfurized at 1050 °C for 4 hrs.

Figure 5. The I-V curves of the photodetector devices measured in the dark (black curves) and under illumination (red curves) for the BaZrS$_3$ films sulfurized at (a) 1050 °C for 4 hrs, and (b) 1050 °C for 2 hrs.
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Figures

Figure 1
Figure 2
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Figure 5
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