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Chalcogenide perovskites—challenges, status, and future prospects

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Abstract

Perovskites dominate the photovoltaic research community over the last two decades due to its very high absorption coefficient, electron and hole mobility. However, most of the reported solar cells constitute organic perovskites which offer very high efficiency but are highly unstable. Chalcogenide perovskites like $BaZrS_3$, $CaZrS_3$, etc. promise to be a perfect alternate owing to its high stability and mobilities. But, till now no stable photovoltaic device has been successfully fabricated using these materials and the existing challenges present in the synthesis of such perovskites are discussed. Also, the basic thermodynamic aspects that are essential for formation of $BaZrS_3$ are discussed. An extensive review on the precedent literatures and the future direction in the $BaZrS_3$ photovoltaic device research is clearly given.

1 Introduction

In the past decade, perovskites have taken over the photovoltaic (PV) research sector, which lead to the dramatic increase of its efficiency to 25.7% over a period of 10 years. Perovskites, which are combination of organic and inorganic halides existing in the perovskite crystal structure. Such structures exhibited very high absorption coefficient and very high electron and hole mobility[1]. These features make these materials to be an ideal for efficient collection of the charge carriers. The evolution of such materials to be monolithically integrated as a top layer in Si tandem solar cells is exhilarating as the efficiency of such cells approaches 32.5%[2]. Hence, for the upcoming few decades, the growth of perovskite technology will be in concurrent with the Si technology.

However, despite of such promising accomplishments, perovskites face many challenges in their long-term stability[3]. The lack of internal stability of such materials and ability to degrade easily with external factors like temperature, pressure, humidity and electric field make the foreseen accomplishments of such structures unproductive. In addition, Si solar cell manufacturers promise a lifetime of almost 25 years, but these issues make the utilization of unstable perovskites in large scale questionable[4]. Finding suitable external encapsulation for such halide perovskites is of recent research interest, but eventually modifying the internal structure of halide perovskite without affecting its properties is of ultimate importance.

Stable chalcogenides like $Cu(In,Ga)Se_2$ (CIGS) and other evolving materials like Cu_2ZnSnS_4 (CZTS), Ag_2ZnSnS_4 (AZTS), etc. are promising materials to be a PV absorber but some of the crystallographic factors limits the performance of such materials[5, 6]. Nevertheless, the stability of such structures are unquestionably superior when compared to that of the halide perovskites. However, such chalcogenides have voltage losses due to the defects present in these materials degrades its promise to be a perfect PV absorber material thus far[7].

Thus, by effectively combining the advantages of both these technologies i.e. stability from the chalcogenides and defect tolerance with high performance from the halide perovskites, a new promising family of materials chalcogenide perovskites which are chalcogenide materials existing in the perovskite crystal structure is evolved[8]. Such materials appear to satisfy the key requisites of a highly efficient PV absorber including superior stability and high luminescence[9]. But manufacturing chalcogenide perovskites and creating uniform films impose few critical challenges like high temperature phase formation and tolerance factor limitations for the existence of perovskite structures. This article discusses in detail some of these key challenges involved in fabrication of such materials. In addition, a small review on the synthesis and performance of the most promising candidate $BaZrS_3$ to highlight the prospects of these materials is given.

2 Chalcogenide perovskites—structural factors

Like perovskites, chalcogenides perovskites exist in ABX_3 form (where X = S, Se and A, B are metals with a total oxidation state of 6^+) are quite environmentally safe than lead halide perovskites. According to Tiwari et al.[10], ABX_3 can crystallise in the desired cubic or pseudo-cubic perovskite structure (types P, N, H, T, and O). The crystal structures of all the five different classes of distorted perovskites are shown in Fig. 1. Out of all the 5 different classes, only type P is distorted perovskite structure but all other structures are non-perovskites.

(Color online) Possible unit cell structures of chalcogenide perovskites[10].

Fig. 1. (Color online) Possible unit cell structures of chalcogenide perovskites[10].

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Not all the metals that satisfy the above condition should form a perovskite structure. But, their ionic radii should satisfy the conditions below[10]:

$$\text{Tolerance factor}\left(t\right)=\frac{r_{\rm A}+r_{\rm X}}{\sqrt{2}\left(r_{\rm B}+r_{\rm X}\right)}\quad(0.7t1.1), \tag{1}$$

$$\text{Octahedral factor}\left(\mu\right)=\frac{r_{\rm B}}{r_{\rm X}}\quad(0.44\mu0.9). \tag{2}$$

The tolerance factor is a factor that determines how much the unit cell is distorted. For perfect ABX_3 unit cell, the tolerance factor will be 1. Lower tolerance factor is an indication that distorted perovskite crystal structure with tetragonal, orthorhombic, and rhombohedral structures. Higher tolerance factor ($t > 1.1$) indicates that the cation A is too large for the structure to form stable perovskite[11].

For oxides, due to the small size of anion (r_O = 1.40 Å), the number of possible elements that can form ABO_3 crystal structure with the desired t and μ are very large. But, in case of sulfides and selenides (r_S = 1.84 Å and r_{Se} = 1.98 Å) due to the large ionic radii, a relatively large cation can occupy site A to yield desired t, but there are very few possibilities that can yield the desired μ values[9, 12]. In ABS_3, heavy alkali cations like Ba^{2+}, Sr^{2+}, and Ca^{2+} are the most suitable candidates for position A and for cation B, Ti, Zr, Hf, Sn are the most optimum candidates due to their stable oxidation state of 4+. Even for all the above combinations, the μ value is below the threshold, a maximum value of 0.39 is observed for $AZrS_3$. Among the suitable cations for A, Ba^{2+}, and Ca^{2+} are the most suitable[10].

3 Density functional theory (DFT) based calculations on chalcogenide perovskites

Significant results are already pre-exists in studying the stability of various ABX_3 compounds and determining their properties using DFT. Korbel et al.[13] analysed over 32 000 ABX_3 combinations (oxides, sulfides, selenides) and determined the ground state energies of the compounds through high throughput approach. The calculated energies are found to be much higher than the results obtained elsewhere because he simulated these combinations for a cubic phase with only five atoms and having only one distortion element present. In case of sulfides, Kuhar et al.[14] study 705 structures with ABS_3 form, but the obtained energy levels are not in agreement with the experimental results. Sophia et al.[9] has analysed all the reported DFT results and summarized in two different values, H_f is the formation energy of ABX_3 with respect to competing phases and H_g is the formation energy with respect to ground state. They summarized the results using

$$H_{\rm f}=E_{\rm ABX_3}^{\rm perovskite}-E_{\rm BX_2}-E_{\rm AX}. \tag{3}$$

$$H_{\rm g}=E_{\rm ABX_3}^{\rm perovskite}-E_{\rm ABX_3}^{\rm groundstate}. \tag{4}$$

The results reported by them are summarized in Fig. 2. If both H_f and H_g of a material is positive, then ABX_3 structure it leads to will be unstable which makes the synthesis impossible. But, through practice, some of the unstable phases can be obtained, if H_f does not exceed 200 meV·f·u^{-1} and H_g does not exceed 50 meV·f·u^{-1}. The difference between these energies, $H_f - H_g$, determines the stability of the ABX_3 ground state against decomposition irrespective of its crystal structure. The structures which are potentially stable according to Sophia et al. are highlighted in green in Fig. 2.

(Color online) Formation energies of chalcogenide perovskite with respect to competing phases (Hf) and ground state formation energy (Hg).

Fig. 2. (Color online) Formation energies of chalcogenide perovskite with respect to competing phases (H_f) and ground state formation energy (H_g).

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According to the above results, for Ba, Sr, and Ca in the site A, Hf and Zr are the identical for B. These structures will be stable according to Sophia et al. and such structures have already been fabricated with ease. So, in this work all the precedent synthesis strategies adopted in fabrication of $BaZrS_3$ is discussed in detail.

4 Properties of $AZrS_3$ (A = Ba, Sr, Ca)

Crystal structures of $BaZrS_3$, $CaZrS_3$, and $SrZrS_3$ are experimentally reported to be $GdFeO_3$ distorted perovskite structure with pnma space group. The Zr atom forms a distorted octahedron with the S atoms, while the A (Ba, Ca, Sr) atoms form a cuboctohedron with the S atoms[15]. Majumdar et al.[16] has theoretically predicted the angle of tilting for all the above mentioned perovskite structures. It was reported that for $CaZrS_3$ and $SrZrS_3$, the octahedrons increases on applying the pressure of 15 GPa. But, in contrast, the tilt of octahedron decreases for $BaZrS_3$. The unit cell parameters of the perovskites at various pressures is given in Table 1.

Liu et al.[17] has theoretically calculated all the photoactive properties of $AZr(SSe)_3$ (Ba, Ca, and Sr). The estimated bandgaps of $AZr(SSe)_3$ structures with varying S and Se ratios are shown in Table 2.

Table 1

Computed unit cell parameters of $AZrS_3$ (A = Ca, Sr, Ba) at 0 and 15 GPa[16].

System	At 0 GPa			At 15 GPa		
	a	b	c	a	b	c
$CaZrS_3$	7.07	9.64	6.57	6.87	9.16	6.01
$SrZrS_3$	7.16	9.83	6.77	6.96	9.41	6.15
$BaZrS_3$	7.27	10.16	7.11	6.95	9.79	6.55

Table 2

Estimated bandgap of various $AZr(SSe)_3$ (A = Ba, Ca, Sr) with varying S, Se ratios[17].

Compound	E_g (eV)		
	Ba	Ca	Sr
$AZrS_3$	1.79	1.98	1.99
$AZrS_2Se$	1.55	1.66	1.66
$AZrSSe_2$	1.51	1.52	1.58
$AZrSe_3$	1.34	1.40	1.46

Table 3

Electronic properties of $AZr(SSe)_3$ (A = Ba, Ca, and Sr)[17].

Compound	m_e^* (m_0)	m_h^* (m_0)	ε	E_b (meV)
$CaZrS_3$	0.535	0.686	0.30177	
$CaZrS_2Se$	0.571	0.601	0.29367	
$CaZrSSe_2$	0.449	0.667	0.26850	
$CaZrSe_3$	0.507	0.564	0.26748	
$SrZrS_3$	0.522	0.778	0.31285	
$SrZrS_2Se$	0.483	0.581	0.26463	
$SrZrSSe_2$	0.523	0.938	0.33671	
$SrZrSe_3$	0.516	0.594	0.27753	
$BaZrS_3$	0.534	0.849	0.32890	
$BaZrS_2Se$	0.456	0.610	0.26163	
$BaZrSSe_2$	0.523	0.938	0.33672	
$BaZrSe_3$	0.500	1.097	0.34365	

The bandgap of the structures are found to be increasing as the concentration of S is increasing. Also, comparatively, $BaZr(SSe)_3$ structures show a much lower bandgap when compared to the Ca and Sr based structures. These results suggests us that bandgap of the structures increases as the ionic radius of A decreases. The band structures shown in Fig. 3 also clearly confirm the direct bandgap of these semiconductors. The maximum absorption coefficient of these structures are observed around 6 x 10^5 cm^{-1} suggesting that these structures are most ideal for photovoltaic applications.

(Color online) Band structures for AZrS3 (A = Ba, Sr, Ca)[17] (Reproduced with permission from the Royal Society of Chemistry).

Fig. 3. (Color online) Band structures for $AZrS_3$ (A = Ba, Sr, Ca)[17] (Reproduced with permission from the Royal Society of Chemistry).

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The partial density of states (PDOS) of $AZrS_3$ (A = Ba, Sr, Ca) structures are shown in Fig. 4. The top of the valence bond arises due to the Zr-4d orbitals while the bottom of the conduction band arises due to the S-3p orbitals. The contributions of the A atoms are present only on the band edges. The bandgap changes in all these compounds are due to the change in Zr−S bond length in each case.

(Color online) PDOS for AZrS3 (A = Ba, Sr, Ca)[17] (Reproduced with permission from the Royal Society of Chemistry).

Fig. 4. (Color online) PDOS for $AZrS_3$ (A = Ba, Sr, Ca)[17] (Reproduced with permission from the Royal Society of Chemistry).

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The electron and hole effective mass of $AZr(SSe)_3$ (A = Ba, Ca, and Sr) are shown in the Table 3. These results clearly suggest that the effective mass of the holes are significantly higher when compared to the mass of electrons. Also, the exciton binding energy of these structures decreases as Se increasese in the compound.

The formation energies of $AZr(SSe)_3$ (A = Ba, Ca, and Sr) are shown in the Fig. 5. It is found that selenides are easier to form than the sulfides due to their very low formation energy. These formation energies are calculated by Liu et al. considering that the crystal is at 0 K.

(Color online) Formation energies of AZr(SSe)3 (A = Ba, Ca, and Sr)[17] (Reproduced with permission from the Royal Society of Chemistry).

Fig. 5. (Color online) Formation energies of $AZr(SSe)_3$ (A = Ba, Ca, and Sr)[17] (Reproduced with permission from the Royal Society of Chemistry).

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Meng et al.[18] conducted an exhaustive investigation into the formation energies and transition energy levels of intrinsic point defects in $BaZrS_3$. This study is pivotal for identifying growth conditions for the preferential generation of desired beneficial defects while mitigating the deleterious deep-level defects, thereby enhancing the performance characteristics of $BaZrS_3$ perovskites.

The researchers systematically examined twelve intrinsic point defects, encompassing antisite substitutions, interstitials, vacancies, and cation substitutions. By employing rigorous computational techniques, they determined the transition energies associated with each defect, their respective acceptor-like and donor-like nature, denoted by red and blue highlights, respectively as shown in Fig. 6.

(Color online) Defect energy states for possible defects in BaZrS3[18] (Reprinted with permission from Meng et al. Copyright [2016] American Chemical Society).

Fig. 6. (Color online) Defect energy states for possible defects in $BaZrS_3$[18] (Reprinted with permission from Meng et al. Copyright [2016] American Chemical Society).

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Significantly, among the investigated defects, only five yielded deep-level characteristics: S_{Zr}, S_{Ba}, Zr_S, S_i, and Zr_i. Conversely, the remaining defects act as shallow acceptors or shallow donors. These findings hold considerable significance owing to the profound impact deep-level defects that exert on material performance.

Meng et al. found that near-stoichiometric conditions represent an optimal regime for the synthesis of $BaZrS_3$ perovskites. Such conditions effectively mitigate the formation of deep-level defects while preserving an appropriate charge carrier density, thereby enhancing the material's overall performance.

Nishigaki et al.[19] synthesized four different distorted chalcogenide perovskites $BaZrS_3$, $SrZrS_3$, $BaHfS_3$, and $SrHfS_3$ and also used DFT to calculate the absorption edge of the structures. From Figs. 7(a) and 7(b), the absorption edge of the chalcogenide perovskites is found to be superior to the halide perovskites such as $MAPbI_3$, GaAs, and CISe. It was concluded that chalcogenide perovskites offer excellent stability and very high absorption when compared to the organic perovskites.

(Color online) (a) Absorption spectra of the chalcogenide perovskites. Open circles represent experimental data and solid lines corresponding to DFT result. (b) Comparison of absorption coefficient of chalcogenide perovskites with traditional PV absorbers[19] (Reproduced with permission from the John Wiley and sons).

Fig. 7. (Color online) (a) Absorption spectra of the chalcogenide perovskites. Open circles represent experimental data and solid lines corresponding to DFT result. (b) Comparison of absorption coefficient of chalcogenide perovskites with traditional PV absorbers[19] (Reproduced with permission from the John Wiley and sons).

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Nishigaki et al.[19] also analysed the performance of $BaZr_{0.95}Ti_{0.05}S_3$ as a top cell in a perovskite/c-Si tandem cell configuration. A maximum efficiency of 38.7% was achieved which was very high when compared to the halide/perovskite tandem cells constructed before[20]. A schematic diagram of the device structure and the performance of the tandem cell with respect to thickness is shown in Figs. 8(a)−8(c).

(Color online) (a) Structure of perovskite/c-Si tandem cell. (b) Quantum efficiency of top and bottom cell. (c) Variation of efficiency with respect to thickness of the perovskite[19] (Reproduced with permission from the John Wiley and sons).

Fig. 8. (Color online) (a) Structure of perovskite/c-Si tandem cell. (b) Quantum efficiency of top and bottom cell. (c) Variation of efficiency with respect to thickness of the perovskite[19] (Reproduced with permission from the

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5 $BaZrS_3$

Already $BaZrS_3$ is synthesized through techniques like pulsed laser deposition, nanoparticles based approach, solid state reaction, chemical vapour deposition etc., till now. But, all these synthesis routes involve formation of $BaZrS_3$ through either of the two reactions given below.

From the sulfide precursors,

$$BaS + ZrS_2 \rightarrow BaZrS_3. \quad (5)$$

From the oxide precursors

$$BaCO_3 + ZrO_2 \rightarrow BaZrO_3 + CO_2 \xrightarrow{CS_2/H_2S} BaZrS_3. \quad (6)$$

Table 4

Reported synthesis strategies adopted for synthesis of $BaZrS_3$.

S.No.	Author	Synthesis route	Outcomes
1	Hahn and Mutschke [21]	Binary sulphides reaction at a very high synthesis temperature	Ternary $BaZrS_3$ formed at the boundary of two binary phases, hinder further formation of the ternary phase.
2	Leleiveld et al. [22]	Sulfurize a mixture of $BaCO_3$ and ZrO_2 in H_2S environment at 1373 K	Formation of $BaZrS_3$ having a structure identical to gadolinium orthoferrite upon annealing for 24 h.
3	Clearfield et al. [23]	Sulfurization	Temperatures from 950 to 1200°C at various time periods from 4 to 24 h.
4	Niu et al.[25]	Solid state reaction	Iodine was used to catalyze the reaction and reduce the synthesis time.
5	Xu et al.[26]	Improved sulfurization technique and the conversion rate was proposed as an indicator of the sulfurization level	A new sulfurization technique to raise the chemical potential of CS_2 is used.
6	Wei et al.[27]	Ball milling, followed by sulfurization	Synthesized Ti alloyed $Ba(Zr_{1-x}Ti_x)S_3$ powders with x from 0 to 0.1. Structural integrity of the distorted chalcogenide phase is retained till 4%.

S.No.	Author	Synthesis route	Outcomes
7	Sharma et al.[28]	Ti-alloyed $BaZrS_3$ films were obtained by sulfurization of Ti-alloyed $BaZrO_3$ films	$BaZrO_3$ films were sulfurized in a 3 zone furnace with CS_2 and N_2 as carrier gas.
8	Ravi et al.[30]	Solid-state synthesis	$BaZrS_3$ NCs are first prepared using a solid-state synthesis route, and the subsequent surface modifications lead to a colloidal dispersion of NCs in both polar N-methyl-2-pyrrolidinone and non-polar chloroform solvents.
9	Yu et al.[32]	Pulsed laser deposition of a $BaZrS_3$ target	Synthesis of $BaZrS_3$ thin films at temperatures as low as 500 °C, this is achieved by changing the chemical reaction pathway from sulfurization of oxide perovskites to crystallization of pulsed laser deposited amorphous $BaZrS_x$ films.
10	Comparatto et al.[33]	Sputtering, Ba−Zr precursor films capped by SnS, sulfurized at under 600 °C for 20 min	The partial pressure of sulfur was found to be the key factor in determining the diffusion and crystallization of the precursors.
11	Pradhan et al.[34]	Solution processing	With a sulfurization at 575 °C for 20 min, the molecular precursors converted into single phase thin films. Increasing sulfurization time results in more intense and higher energy photoluminescence emissions.
12	Vincent et al.[35]	Solution processing	High-quality thin films of large-grain $BaZrS_3$ perovskites are prepared by solution processing at moderate temperatures. The study discovered that a barium polysulfide liquid flow is crucial for the fast synthesis of the perovskite, and this method was effectively applied to the $BaHfS_3$ perovskite as well.
13	Ramanandan et al.[36]	Two-step synthesis mechanism of $BaZrS_3$, involving an intermediary amorphization phase of $BaZrO_3$	They identify sulfur species diffusion within the film as the rate-determining step. The conversion of H_2S to the sulfide phase varies significantly with processing temperature.
14	Dhole et al.[37]	Polymer-assisted deposition	This technique involved the deposition of cation precursor films chelated with polymer, followed by sulfurization in a mixed atmosphere of carbon disulfide and argon.
15	Romagnoli et al.[38]	Simple synthetic approach under relatively mild conditions (T = 500 °C) and is complete in a few hours	By combining BaS, Zr(Hf), and S powders for 20 min in mortor and pestle and sulfurization.

Even though these equations make it easy to see how $BaZrS_3$ is made, it is hard to make high-quality $BaZrS_3$ because it grows poorly at temperatures above 1000 °C and takes many hours or days to respond. These unconventional conditions make the PV devices formation extremely challenging. These challenging synthesis conditions might be due to the following reasons.

Several studies confirmed that formation of $BaZrS_3$ by reaction of binary sulphides demand a very high synthesis temperature. For example, Hahn and Mutschke[21] discovered that even though the ternary $BaZrS_3$ phase is more stable than the binary ZrS_2 and BaS, but these two phases does not react until 900 °C. They also concluded that the ternary $BaZrS_3$ formed at the boundary of two binary phases, hindering further formation of the ternary phase because it reduces the diffusion of the precursors and a lot of thermal energy is required to overcome this kinetic diffusion barrier.

Another strategy for synthesizing $BaZrS_3$ is to sulfurize a mixture of $BaCO_3$ and ZrO_2 in H_2S environment. But, this process also demands a synthesis temperatures of 1373 K. Leleiveld et al.[22] utilized this route to synthesize $BaZrS_3$ but the sulfurization was carried for seven days. Neutron diffraction results reveal the formation of $BaZrS_3$ having a structure identical to gadolinium orthoferrite ($GdFeO_3$). The estimated lattice parameters for the structures are found to be (a, b, c) = (0.70599, 0.99813, 0.70251 nm) with a space group of Pnma and Z = 4. Using the same route, Clearfield et al.[23] fabricated $BaZrS_3$ at temperatures from 950 to 1200 °C at various time periods from 4 to 24 h. Structural characterizations revealed the lattice parameters as (a, b, c) = (0.7037, 0.9983, 0.7050 nm) and they exhibited a distorted perovskite structure.

Using first principles calculation, Sun et al.[24] has evaluated the optoelectronic properties of various ABX_3 compounds, where A represents a 2+ cation and B denotes a 4+ cation and X is either sulphur or selenium. They also estimated the bandgap of the structures. From these structures, they have discovered that $BaZrS_3$, $CaHfSe_3$, $CaZrSe_3$, and $CaTiS_3$ will be ideal for photovoltaic applications owing to their optimal bandgap and very high absorption coefficient greater than 10^5 cm^{-1}.

The major advantage of such structures was long term stability and ability to tolerate heat up to 400 °C. In order to understand that, Niu et al.[25] synthesized and evaluated the thermal stability of $BaZrS_3$, Ba_2ZrS_4, α-$SrZrS_3$, β-$SrZrS_3$, and $Ba_3Zr_2S_7$. By studying differential scanning calorimetry and thermogravimetric analysis (DSC-TGA) of such structures, they proved that perovskite chalcogenides are highly stable in air up to a temperature of 550 °C.

Xu et al.[26] studied the thermal stability of $BaZrS_3$ by heat treating at air and at very low pressure. They concluded that $BaZrS_3$ was stable till 400 °C in air and in a low pressure of 10^{-1} Pa, it was stable till 700 °C. These results are crucial to understand the stability of such structures under post deposition treatments that may be essential during the fabrication of photovoltaic devices with $BaZrS_3$.

The bandgap of $BaZrS_3$ can be tuned by alloying with various elements like Ti, Hf, etc. In order to study the effects of Ti alloying on $BaZrS_3$, Wei et al.[27] synthesized $Ba(Zr_{1-x}Ti_x)S_3$ powders with varying x values between 0 and 0.1. By alloying 4% of Ti into $BaZrS_3$, the bandgap can be lowered to 1.51 eV from 1.78 eV. This reduction in bandgap can lead to significant increase in the solar cell efficiency. Structural integrity of the distorted chalcogenide phase is retained till 4%, but while doping at higher concentration, the structure is observed to destabilize and binary sulphides tend to form. This study on band gap tailoring using Ti-alloying of $BaZrS_3$ is unique as it drives $BaZrS_3$ towards the solar cell based devices.

A similar strategy was utilized by Sharma et al.[28] in obtaining Ti alloyed $BaZrS_3$ films using chemical vapour deposition method. They observed that upon 6% Ti alloying, the bandgaps lowered from 1.75 to 1.4 eV, which is the most optimum bandgap corresponding to the Schockley−Queisser limit. Alloying concentrations above 6% lead to degradation of the disordered perovskite phase and phase segregation which is in agreement with their theoretical results too. Titanium-alloyed $BaZrS_3$ thin films can serve as an excellent option for optoelectronic devices because of their ideal bandgap, great environmental stability, and non-toxic behaviour.

The stability of photodetectors fabricated using $BaZrS_3$ and $MAPbI_3$ was computed and calculated by Gupta et al.[29]. They observed that upon operation in humid environments, organic perovskite’s photoresponsivity degraded by 95% in four weeks, while the inorganic perovskite $BaZrS_3$ retained 60% of the initial performance. This shows that chalcogenide perovksites degrade at a much slower rate which is due to the very low anion migration rate in them when compared to $MAPbI_3$. The discovery provides both theoretical reasoning and experimental evidence supporting the environmental viability of $BaZrS_3$. This chalcogenide perovskite emerges as a highly promising candidate for optoelectronics due to its notable absence of toxic lead and inherent sustainability.

Cubic $BaZrS_3$ nanocrystals of edge lengths between 40 and 60 nm are synthesized by Ravi et al.[30] through solid-state synthesis. The structural stability of the nanostructures is investigated through XRD and XAFS (X-ray absorption fine structure) at temperatures between 15 and 613 K. They also tuned the surface chemistry of the nanostructures to make a stable colloidal suspension in polar solvent (N-methyl-2-pyrrolidinone) as well as the non-polar solvent (chloroform). Spin coated thin films of the colloids are fabricated and the hole mobility of 0.059 $cm^2{\cdot}V^{-1}{\cdot}s^{-1}$ and electron mobility of 0.017 $cm^2{\cdot}V^{-1}{\cdot}s^{-1}$ are found and the nanocrystals show both p and n type ambipolar transistors behaviour.

Pulsed laser deposited amorphous $BaZrO_3$ precursors are sulfurized by Márquez et al.[31] in 5% H_2S + Ar mixture at temperatures from 700 to 1100 °C for 30 min to obtain $BaZrS_3$ −$BaZrO_3$ perovskite films. S concentration in the films is found to be increasing as the sulfurization temperature is increased signifies the incorporation of S into $BaZrO_x$. The photographs, FESEM images and XRD patterns of the films are shown in Figs. 9(a)−9(c).

(Color online) (a) Photographs, (b) surface morphology, and (c) XRD patterns of the BaZrS3 films prepared at various sulfurization temperatures[31] (Reprinted with permission from Marquez et al. Copyright [2021] American Chemical Society).

Fig. 9. (Color online) (a) Photographs, (b) surface morphology, and (c) XRD patterns of the $BaZrS_3$ films prepared at various sulfurization temperatures[31] (Reprinted with permission from Marquez et al. Copyright [2021] American Chemical Society).

Also, the S incorporation saturates at temperatures above 1000 °C and through this route a maximum S/(S + O) ratio of 0.85 is achieved showing that the oxide phase is preserved in the thin film in a trace amount.

Amorphous $BaZrS_3$ films were prepared using pulsed laser deposition of a $BaZrS_3$ target by Yu et al.[32]. The films are crystallized by processed in CS_2 at temperatures varying from 500 to 900 °C. Phase purity was observed in all the films and specifically at 550 °C the films were highly crystalline with very low surface roughness less than 0.6 nm. They also developed prototype photodetector systems and FET devices using the fabricated $BaZrS_3$ films.

Through sputtering, Ba−Zr precursor films capped by SnS were synthesized by Comparatto et al.[33] and sulfurized at under 600 °C for 20 min. The partial pressure of sulfur was found to be the key factor in determining the diffusion and crystallization of the precursors. Although, presence of trace Sn was observed in the films, but the crystallinity of the films was found to be superior. This study also emphasized the importance of a capping layer SnS on the Ba−Zr precursors which prevented the Ba−Zr films from oxidation.

Through solution processing Pradhan et al.[34] synthesized $BaZrS_3$ and $BaHfS_3$ films. With a sulfurization at 575 °C for 20 min, the molecular precursors converted into single phase thin films. This accomplishment not only reduced the sulfurization temperature mutlifold. This process significantly eased the fabrication challenges that were faced by the research community.

Vincent et al.[35] used a solution processing approach to understand the underlying mechanism and develop methodologies for producing high-quality thin films of large-grain $BaZrS_3$ perovskites at moderate temperatures. The study discovered that a barium polysulfide liquid flow is crucial for the fast synthesis of the perovskite, and this method was effectively applied to the $BaHfS_3$ perovskite as well. The findings provide information on precursor choice, sulfurization temperature ranges, and reaction conditions that are likely to promote the development of large-grain chalcogenide perovskite, which is critical for producing device-grade thin films.

Ramanandan et al.[36] elucidated the two-step synthesis mechanism of $BaZrS_3$, involving an intermediary amorphization phase of $BaZrO_3$. They identify sulfur species diffusion within the film as the rate-determining step. The conversion of H_2S to the sulfide phase varies significantly with processing temperature. Despite Zr-rich precursors, stoichiometric $BaZrS_3$ (1 : 1 : 3) predominates, accompanied by ZrO_2 as a secondary phase, in contrast to the versatile non-stoichiometric compositions observed in chalcopyrites and kesterites. $BaZrS_3$ stands out from other chalcogenides in this aspect. The findings of this study pave the way for further optimization of $BaZrS_3$ synthesis processes, thereby expanding the potential applications of this material in the future.

Dhole et al.[37] effectively fabricated thin films of $BaZrS_3$ utilizing a polymer-assisted deposition (PAD). This technique involved the deposition of cation precursor films chelated with polymer, followed by sulfurization in a mixed atmosphere of carbon disulfide and argon. Through X-ray diffraction (XRD) and Raman spectroscopy analyses, the study confirmed the formation of single-phase polycrystalline $BaZrS_3$ thin films at 900 °C. These $BaZrS_3$ films exhibited a photoluminescence peak at approximately 1.80 eV and demonstrated the capability to generate a photogenerated current upon light illumination at a wavelength of 530 nm.

Romagnoli et al.[38] produced $BaZrS_3$ by combining BaS, Zr(Hf), and S powders in a 1 : 1 : 3 molar ratio in an agate mortar for 20 min in air. The powder was then transported through a sealed ampoule and heated in a muffle furnace at 500 °C overnight to produce phase pure $BaZr_xHf_{1-x}S_3$ nanoparticles. The ability to change the band gap of the material from 1.78 to 2.11 eV by adjusting the Hf/Zr ratio is fascinating. The precedent literatures discussed in this article are summarized in Table 4.

6 Predicted device structures using SCAPS-1D simulator

Till now no experimental reports on application of $BaZrS_3$ is reported, but in recent times many reports towards identifying various constituent materials that are most optimal for the $BaZrS_3$ photovoltaic devices using SCAPS-1D are available. Mercy et al.[39] has clearly summarized all the precedent literatures and their reported configurations and device performances. The photovoltaic device performances of all the precedent literatures are summarized in Table 5.

Among all the configurations reported till now, $FTO/ZrS_2/BaZrS_3/SnS/Pt$ device configuration is reported to be more appropriate. A maximum efficiency of 28.17% was reported which was very close to the theoretical maximum efficiency of 30.17% for $BaZrS_3$ perovskite[45]. So, the experimental researches can use this structure for their initial fabrication of devices.

Table 5

Reported solar cell device structures for $BaZrS_3$ photovoltaics.

Device Structure	Estimated solar cell characteristics				Reference
	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	Efficiency (%)	
$FTO/TiO_2/BaZrS_3$/Spiro-OMeTAD/Au	1.21	16.54	86.26	17.29	[40]
$FTO/TiO_2/BaZrS_3/Cu_2O/Au$	1.16	12.24	87.13	12.42	[41]
$FTO/TiO_2/BaZrS_3/CuSbS_2/W$	1.00	22.57	73.7	17.13	[42]
$FTO/TiO_2/BaZrS_3$/Spiro-OMeTAD/Au	0.70	22.00	79.40	12.12	[43]
AZO/i-ZnO/CdS/$BaZrS_3$/a-Si	1.31	19.08	78.88	19.72	[44]
$FTO/TiO_2/BaZrSe_3$/Spiro-OMeTAD/Au	0.72	46.65	77.32	25.84	[43]
$FTO/TiO_2/Ba(Zr_{0.87},Ti_{0.12})S_3/Cu_2O$/back contact	1.09	26.57	85.78	24.86	[27]
AZO/i-ZnO/CdS/$Ba(Zr_{0.95},Ti_{0.05})S_3$/a-Si	1.26	27.06	88.47	30.06	[44]
$FTO/ZrS_2/BaZrS_3/SnS/Pt$	1.18	29.74	80.15	28.17	[39]
$FTO/ZrS_2/Ba(Zr_{0.96},Ti_{0.04})S_3/SnS/$ Pt	1.18	32.26	84.94	32.58	[39]

7 Conclusions and future scope

Till now the precedent literatures discussed shows promise on reducing the synthesis of $BaZrS_3$, but no photovoltaic devices are constructed till now. This is majorly due to the lack of knowledge of the proper solar cell structure that is needed. Many simulation studies already showed promising cell structures similar to that of CZTS, but a practical analysis of such photovoltaic devices are yet to be studied in detail. Also, the defect engineering, bandgap gradient structures and post deposition annealing which are promising strategies in CIGS and CZTS based devices can be adopted here.

Potential synthesis routes need to be identified to fabricate $BaZrS_3$ at low temperature through solution processed techniques. This can lead to fabrication of $BaZrS_3$ over flexible photovoltaic applications. Along with $BaZrS_3$, other potential chalcogenide perovskites need to be researched for their photovoltaic performance which can enlighten the stability and usefulness of these structures in energy conversion. Also, possibilities of integrating these perovskites into tandem structures with other promising photovoltaic technologies can be a potential area of research.

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