Tin and germanium substitution in lead free perovskite solar cell: current status and future trends

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Abstract. Tin and germanium-based perovskite solar cell is gaining interest in lead-free perovskite solar cells as it is less toxic as compared to lead but possess almost all the characteristics of a perfect solar cell materials. Within 5 years, the reported efficiency of tin-based solar cells has increased from 6.4% to 9%. Although facing with stability issues as it is easily oxidised in ambient air, several studies have proven that the stability issues can be reduced. One of it is by using cesium as the ‘A’ cation. On the other hand, although studies on germanium-based perovskite solar cells are rarely conducted, promising results are shown when it is alloyed with tin producing narrower bandgaps and better stability owing to the protection of the GeO2 surface layer.

1 Introduction

Perovskite solar cell (PSC) has shown notable progress since its first debut in 2009 [1]. Ever since then, the PCS has shown remarkable breakthrough and advances rapidly as the next generation solar cells. PSC consist of a perovskite compound with chemical formula of ABX3 where A is an organic cation (methyl-ammonium ‘MA’ and/or formamidinium ‘FA’), B a divalent metal ion (Pb2+, Bi2+, Sb2+, Sn2+, Ge2+ etc.) and X a halide ion (F-, I-, Br- or Cl-). The typical perovskite structure is depicted in Fig. 1 [2]. Since the fabrication of PSC is solution based, wide range of alteration is possible that include band-gap and conductivity-type modification through doping and/or alloying resulting in various perovskite structures [3, 4]. Direct substitution of the cations or anions will subsequently lead to distortion to the perovskite structure as the formability of this structure is based on the ratio between the cations and anions (A:X and B:X) [5, 6]. The Goldschmidt tolerance factor (GTF) is used to determine the crystal structure of the perovskite materials and is given as:

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where $r$ is the ionic radius of A-cation, B-cation and X-anion.  An ideal perovskite material should have a perfect cubic structure with $t$ of 0.8 to 1 [7-9]. When the tolerance factor is lower than 0.8 or higher than 1, distorted octahedral structure is formed that will result in loss in symmetry thus affecting the electronic properties of the material [10].

\begin{equation}
    t = \frac{r_A + r_X}{\sqrt{2(r_B + r_X)}}
\end{equation}

Fig. 1. Typical crystal structure of a perovskite with A, B and X ions [2]

With lead (Pb) as the active material, the power conversion efficiency (PCE) of PCS has escalated from merely 3.81% [1] to 23.7% [11] in less than a decade. However, the major obstacle in commercialization of Pb-based PCS is the toxicity of Pb that poses threat to the environment as well as human health [12]. Numerous studies have been conducted by various researchers in order to find the prospective substitute for Pb while maintaining the high efficiency and stability.

2 Approaches to lead-free perovskite solar cell

An ideal PSC material to replace Pb should be less toxic while still maintaining its high stability and excellent electrical properties. Besides that, these materials should also possess all the necessary characteristics of a perfect PCS i.e. having narrow direct bandgap, high light absorption coefficients, high charge carrier mobilities, low exciton-binding energies, long charge-carrier lifetime and long exciton diffusion length [13, 14]. A number of potential metals have been identified based on the Goldschmidt’s model that include the group 14 elements, alkaline earth metals, p-block elements, transition metals and lanthanides (Fig. 2), all of those elements with stable oxidation state of +2. However, those elements with large bandgap (Be$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$), high toxicity (Cd$^{2+}$ and Hg$^{2+}$), high radioactivity and low stability are considered less suitable [15].

Amongst these candidates, the group 14 elements (Sn$^{2+}$, Ge$^{2+}$ and Si$^{2+}$) are most favourable due to their similar electronic configuration to Pb [16, 17]. However, the stability of the +2 oxidation state is decreasing moving up the Periodic Table due to the reduction in inert electron pair effects while the reduction of bandgap is also observed owing to increased ionic characteristics [14].
Fig. 2. Elements to replace Pb in perovskite in the periodic table

3 Tin as substitute for lead in perovskite solar cell

To attain Pb-free PSC, Sn$^{2+}$ was among the first divalent metal considered as an alternative candidate to substitute Pb$^{2+}$ due to the comparable electronic configuration and close effective ionic radius (1.35 Å) as of Pb$^{2+}$ (1.49 Å) [18, 19]. Besides that, Sn-based perovskites also possess lower direct optical bandgap (1.2 – 1.4 eV) and higher charge carrier mobility (10$^2$ – 10$^3$ cm$^2$/V·s) compared to Pb [20-22]. The first reported study on Sn-based PSC was conducted by [23] with PCE of 6.4%. In this study, a mesoporous structure was fabricated. Following the success of this study, several attempts have been conducted to further improve the efficiency of the Sn-based PSC. This include integrating different ‘A’ cation such as MA [24-26], FA [27, 28] and cesium (Cs) [29-31] resulting in a symmetrical 3D structures [22]. Besides that, mixed ‘A’ cation is also employed [32] as it combine the best characteristics of individual cation and boost resistance in normal ambience [14]. A study by [33] reported that addition of “hollow” ethylenediammonium (en) cations enhance the performance and stability of a PSC by improving the film morphology, increasing the bandgap, unit cell volume and carrier lifetime while lowering the trap-state density. The highest efficiency realize by this PSC is 6.63%.

Besides varying the ‘A’ cation, numerous studies were also conducted employing several halide ions ‘X’ namely I\textsuperscript{–}, Br\textsuperscript{–} and Cl\textsuperscript{–}. Reported studies employing I\textsuperscript{–} as the halide ion has shown promising results with highest PCE of 9% using FASnI\textsubscript{3} [34]. A study by [35] has indicated that for Sn-based PSC, the bandgap increases from I\textsubscript{3}, Br\textsubscript{3} and Cl\textsubscript{3}. Although replacement of I\textsuperscript{–} with Br\textsuperscript{–} or Cl\textsuperscript{–} shows improvement in certain composition, the formation of cubic perovskite is difficult either by using Br\textsuperscript{–} or Cl\textsuperscript{–} owing to the smaller ionic radius [36].

The major shortcoming in Sn-based PSC is the stability issue where Sn$^{2+}$ is easily oxidize in ambient conditions into Sn$^{4+}$ that can be observed by the discoloration of the perovskite solution in the presence of oxygen leading to reduction in its photovoltaic properties [37-39]. Although Cs cation is most stable for Sn-based perovskite, the major drawback lies in the low mobility, high minority carrier and the disability to form a fully 3D perovskite structure [13]. Table 1 depicted some of the major studies on Sn-based PSC to date.

| Perovskite type | Bandgap (eV) | J$\text{sc}$ (mA.cm$^{-2}$) | V$\text{oc}$ (V) | FF | PCE (%) | References |
|----------------|-------------|-----------------|--------------|----|--------|------------|
| CsSn$\textsubscript{I}_3$ | 1.30 | 4.80 | 0.42 | 0.22 | 0.90 | [18] |
| MASnI$\textsubscript{3}$ | 1.23 | 16.80 | 0.88 | 0.42 | 6.40 | [23] |
Germanium as substitute for lead in perovskite solar cell

Germanium (Ge) is another potential candidate in lead free PSC as it is in the same group 14 as Pb and Sn. Studies have shown that although Ge possesses similar transport and optical properties as Pb and Sn analogues due to its divalent nature they are hardly been investigated due to its mercurial character in +2 oxidation state [14]. With smaller ionic radius, poor solubility in polar solvent, and relatively wide bandgap (>1.6eV), the PCE for Ge-based PSC to date is still less than 5% [41-43]. Lowest bandgap for PSC is observed when Cs is used as the ‘A’ cation as compared to MA and FA, hence it is anticipated that CsGeX perovskite is more suitable for solar cell application [44, 45]. On the other hand, changing the ‘X’ anion will also increase the bandgap of the PSC with I− showing the lowest bandgap followed by Br− and Cl− [46, 47]. Most studies suggest that in line with the Sn-based PSC, the stability issue is the major concern in Ge-based PSC. Hence further studies are to be carried out either by using tandem structures [15, 19], the introduction of additive [48] or alloying.

Mixed Sn-Ge perovskites for solar cell

Mixed ‘M’ cation has been carried out in mixed Pb:Sn based PSC and has shown promising results [22]. Varying the Pb:Sn ratios will enable tuning in of the bandgap and further increase the stability. The same trend is observed in mixed Sn:Ge based PSC where lower bandgap and better stability can be achieved. A theoretical study by [49] predicted that the preparation of a stable Sn:Ge PSC is possible with higher carrier mobility and better resistance to water penetration. Another study by [50] employing mix Sn:Ge PSC resulted in higher performance of 4.48% PCE compared to 3.31% without Ge. It is believed that passivation of Ge has effectively reduce defects on the surface of the Sn-based perovskite hence reducing recombination and increasing the efficiency. The highest PCE (7.9%) of Sn:Ge-based PSC by far is realised in another study by [51] where addition of Ge is believed to increase the stability of the perovskite structure while reducing the trap density. Hence it is believed that more promising results is anticipated in this area of studies.

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