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To cite this article: Ayu Wazira Azhari *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **957** 012057

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# 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 GeO<sub>2</sub> 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 ABX<sub>3</sub> where A is an organic cation (methyl-ammonium 'MA' and/or formamidinium 'FA'), B a divalent metal ion (Pb<sup>2+</sup>, Bi<sup>2+</sup>, Sb<sup>2+</sup>, Sn<sup>2+</sup>, Ge<sup>2+</sup> etc.) and X a halide ion (F<sup>-</sup>, I<sup>-</sup>, Br<sup>-</sup> or Cl<sup>-</sup>). 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:

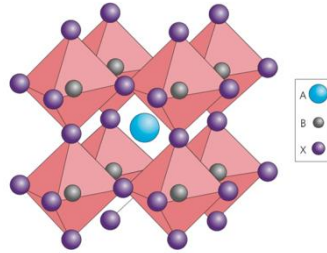
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$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (1)$$

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 of symmetry thus affecting the electronic properties of the material [10].



**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 a 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 ( $\text{Be}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ), high toxicity ( $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ ), high radioactivity and low stability are considered less suitable [15].

Amongst these candidates, the group 14 elements ( $\text{Sn}^{2+}$ ,  $\text{Ge}^{2+}$  and  $\text{Si}^{2+}$ ) 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].



MASnI <sub>3</sub>	1.30	16.30	0.68	0.48	5.23	[24]
MASnIBr <sub>2</sub>	1.75	12.30	0.82	0.57	5.73	[24]
MASnI <sub>3</sub>	1.34	21.40	0.32	0.46	3.15	[25]
FASnI <sub>3</sub>	1.40	22.07	0.465	0.60	6.22	[27]
CsSnIBr <sub>2</sub>	-	17.40	0.31	0.57	3.20	[29]
Cs <sub>2</sub> SnI <sub>6</sub>	-	13.97	0.58	0.42	3.44	[30]
FASnI <sub>2</sub> Br	1.68	6.82	0.467	0.54	1.72	[28]
CsSnBr <sub>3</sub>	1.75	9.10	0.41	0.58	2.17	[31]
MASnI <sub>3</sub>	1.23	26.00	0.232	0.386	2.33	[26]
CsSnI <sub>3</sub>	-	25.71	0.38	0.49	4.81	[40]
enMASnI <sub>3</sub>	1.40	24.28	0.429	0.64	6.67	[33]
(FA) <sub>0.75</sub> (MA) <sub>0.25</sub> SnI <sub>3</sub>	1.33	21.20	0.61	0.63	8.12	[32]
FASnI <sub>3</sub>	-	24.1	0.525	0.71	9.0	[34]

#### 4 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<sup>-</sup> showing the lowest bandgap followed by Br<sup>-</sup> and Cl<sup>-</sup> [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.

#### 5 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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