Improving Tin-Based Perovskite Nanomaterials for Solar Cell Applications

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ABSTRACT

Perovskite solar cells are a cutting-edge technology that have the potential to revolutionize the renewable energy market because of their remarkable affordability and efficiency. Tin-based perovskites have attracted a lot of interest among the many perovskite compositions as a potential substitute for lead-based alternatives. However, issues with stability and efficiency restrict their wider use in solar cells. The goal of this work is to enhance the stability and performance of tin-based perovskite nanoparticles in solar cell applications. It investigates the novel combination of mixed tin-germanium with ethylammonium, formamidinium (FA), methylammonium (MA) and cesium (Cs) to improve the optoelectronic characteristics and environmental resilience of tin-based perovskites solar cells. Our investigation suggested that the mixed compositions with $EA_{0.5}Cs_{0.5}SnGeI_3$ *as the perovskite material were expected to have a theoretical bandgap within the maximum SQ limit (1.34 eV) and ABX3 cubic structure (t = 0.99) suggesting effective charge production and photon absorption. A multidisciplinary strategy involving materials science, engineering, and chemistry is needed to improve tin-based perovskite nanomaterials for solar cell applications, with an emphasis on both performance and economic feasibility. To fully grasp the promise of this exciting technology, further research and innovation will be needed as the industry develops.*

Keywords: SnGe, perovskite, lead-free nanomaterial, binary metal halide, solar cells.

1. INTRODUCTION

Cation engineering (CE), which is standard method for modification and optimization of the composition and/or material of ABX3, where A and B are cations and X is an anion in the crystal structure of perovskite materials, is applied in the development of improved characteristics and functionality of perovskite solar cells (PSCs). Perovskite materials' A, B, and X components may be altered by CE to provide desirable properties such increased charge carrier mobility, greater light absorption, and increased stability [1]. Modifications applied to the A-site cation can change the crystal structure and lattice characteristics of perovskites. As a result, different A-site cations may be used to regulate the bandgap and stability of perovskite materials [2]. Meanwhile, the B-site cation affects the electrical and optical properties of perovskites. By substituting higher stability materials for the metal ions at the B-site, it is possible to modify the bandgap, carrier transport, and defect development in perovskite materials [3].

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The cation arrangement has a significant impact on PSC stability and optoelectronic properties; PSCs are often composed of conventional organic A-cations (FA, MA, and Cs). According to recent studies, adding ethylammonium (EA) to the perovskite structure can increase long-term stability and power conversion efficiency [4]. Several characteristics of EA make it an intriguing alternative. For example, a larger cation than other (2.74 Å) can help to improve the structural stability of the perovskite material. Furthermore, the inclusion of an EA may slow down ion migration, improving the stability of the perovskite layer. Longer carrier lifetimes and greater charge carrier mobilities can result from the EA cation's ability to prevent the creation of defects in the crystal lattice. Reduced recombination losses and more effective charge extraction were two of these aspects that improved the overall performance of the device [5, 6].

CE can potentially be employed to incorporate alloy Ge into Sn-based devices or vice versa, which will improve device performance and reduce the probability of faults [7]. Ge atoms can take the place of Sn atoms in the crystal lattice when Ge is alloyed with Sn-based materials. Because there are no Sn atoms present, there is less chance of vacancies forming as a result of this replacement. Ge is added to the crystal structure to assist fill the voids and minimize flaws. In addition, Ge, more precisely Ge2+, can function as a substitute ion. By preserving the charge balance inside the crystal lattice, this substitution lessens the likelihood of charged defects [8].

The electrical and optical characteristics of a material might be adversely affected by the existence of charged deficiencies [9]. By alloying Ge into Sn-based materials, defects may be reduced and the crystal structure stabilized, which can increase device performance and, indirectly, the optoelectronic properties and stability of Sn-based perovskite can be significantly enhanced [8]. Apart from that, CE may be used to introduce passivating agents or modify surfaces in order to reduce trap states and increase the lifetimes of charge carriers [10]. These passivation techniques have enhanced the performance and stability of Sn-based perovskite devices, showing promising findings [11].

Perovskites can potentially be synthesized with even more control over the material characteristics by mixing mixed A cation with alloyed B cation. Improved stability, increased absorption of light, and optimized charge transport qualities can result from these combinations. The production of mixed-cation perovskites by the alloyed Sn-Ge perovskite structure's incorporation of mixed A-cations (FAMA) is one noteworthy example. Using photoacoustic spectroscopy and ultraviolet-visible spectrophotometry, the electrical and optical properties of the perovskite materials were assessed. The results showed that the materials' bandgap values ranged from 1.40 to 1.53 eV, confirming the theory that mixed A cations with alloyed B cations can be used in solar cell applications [12].

2. MATERIALS AND METHODS

The octahedral factor and tolerance factor of mixed A cations (formamidinium; FA, methylammonium; MA, ethylammonium; EA, caesium; Cs), mixed B cations (tin; Sn, germanium; Ge), and X anion (iodide, I) outline the estimate of hybrid perovskite crystal structure (AxA'1-xByB'1-yX3). The geometry of a crystal structure is described by octahedral factor (Equation 1) and tolerance factor (Equation 2), especially in respect to formations that resemble perovskites. The deviation from a perfect octahedral coordination geometry in B cations with y = 0, 0.25, 0.5, and 1 is measured by the octahedral factor (μ). In the meanwhile, a parameter with x = 0.5 that characterizes the distortion in overall perovskite structures is the tolerance factor (t). The elemental atomic radii of the selected materials, rX, rBB', and rAA' (Equations 3–4), are given in Table 1. Doped cations are identified as A' and B', respectively, whilst the main A and B-cations are marked as A, B. A stable structure is indicated by a μ value greater than 0.41, and the perovskite structure can form and the structure is more likely to be cubic [t = 0.9 to 1].

$$\mu = \frac{r_{BB'}}{r_X} \tag{1}$$

$$t = \frac{r_{AA'} + r_X}{\sqrt{2(r_{BB'} + r_X}} \tag{2}$$

$$r_{AA'} = (x)r_A + (1 - x)r_{A'} \tag{3}$$

$$r_{BB'} = (y)r_B + (1 - y)r_{B'} \tag{4}$$

Table 1 Characteristics of potential materials

Element	**Atomic radii (Å)**
Sn^{2+}	1.15
Ge^{2+}	0.73
FA^{+}	2.53
MA^{+}	2.17
EA^{+}	2.74
Cs^{+}	1.67
I^{-}	2.20

This study also examines the Shockley-Queisser (SQ) limit for Sn-based perovskite solar cells (PSCs) which falls between 1.2 and 1.4 eV with a simple linear interpolation model (Vegard's Law) that assumes a linear relationship between the lattice constant and the band gap of a mixed compound with respect to the compositions (0.5) of the constituents.

3. RESULTS AND DISCUSSION

A theoretically stable structure with $\mu > 0.41$ may be produced by a mixed composition between Sn and Ge at equivalent concentrations and above (<50%), as seen in Figure 1 by an assessment of distortion in the suggested mixed B-cation ($Sn_yGe_{1-y}I_3$; y = 0, 0.25, 0.5, 0.75, 1) due to a process known as substitutional solid solution, the ratio of mixed $Sn_{0.5}Ge_{0.5}$ (rBB' = 0.94 Å) compounds with iodide (rX = 2.2 Å) generate stable structures ($\mu = 0.427$). This indicates that Sn atoms may be substituted with Ge atoms in a crystal lattice as defined by Hume-Rotary laws. Given that Sn and Ge are members of the same periodic table group (Group 14), it is believed that their comparable chemical characteristics contribute to the stable structure. They may substitute for one another in crystal structures without significantly altering them because they have comparable four valence electron configurations in their highest-energy orbitals (Ge; $4s^24p^2$ and Sn; $5s^25p^2$) and similar covalent and metallic bonding behaviors.

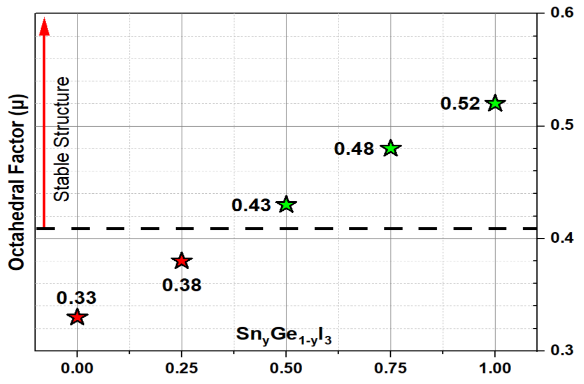

Figure 1. Octahedral factor of SnGe.

Based on ionic size limits for the relevant cations and anions, a formability and stability range for ABX_3 perovskite structures has been empirically determined, suggesting the existence of a cubic-crystalline in ABX_3. Figure 2 depicts an $A_xA'_{1-x}Sn_{0.5}Ge_{0.5}I_3$ with A cation materials consisting of FAMA, FAEA, FACs, MAEA, MACs, and EACs with x at 0.5. Calculated results show that the cubic perovskite structure (t = 0.9 to 1) can be formed with MA/FA/EA doped with $CsSnGeI_3$ (t = 0.93, 0.97, 0.99) respectively, while other compositions (FAMA, MAEA, and FAEA) have a hexagonal structure with the t greater than 1. The nearly cubic structure of $EACsSnGeI_3$ (0.99) in comparison to $FACsSnGeI_3$ (0.97) and $MACsSnGeI_3$ (0.93) may be caused by several of factors, including the comparatively well-matched atomic radii of the I anion, Sn, and Ge cations in the EACs. A slight deviation from the ideal cubic perovskite structure is produced by the X-anions and the balanced size relationship between the A-site and B-site cations [13].

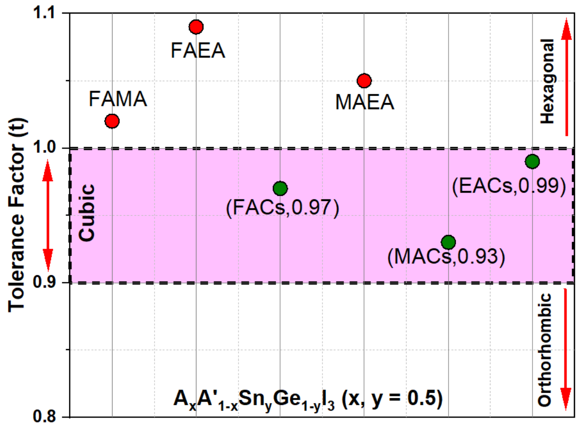

Figure 2. Tolerance factor of mixed cation SnGe.

Given the suggested materials' composition, Vegard's Law is able to provide a preliminary estimate of bandgap energy in the case of novel alloyed perovskites with minimal experimental data [14]. Table 2(a-b) presents the bandgap prediction of $EACsSnGeI_3$, $FACsSnGeI_3$, and $MACsSnGeI_3$, which indicate the theoretical estimation of mixed cations SnGe from pure single Sn and Ge mixtures. This is achieved by considering into account the calculated tolerance factor in doped CsSnGeI3 into FA, MA, and EA, which can resemble the structure of perovskite.

The SQ limit, which is based on a single p-n junction and represents the theoretical maximum efficiency that may be achieved, is established by the bandgap of the material that is being employed. According to the SQ limit, the absorber material's bandgap must match the energy of photons in the solar spectrum for optimal efficiency to occur [15]. For Sn-based perovskites, a bandgap of around 1.2 to 1.4 eV is thought to be ideal since it enables effective absorption of a broad range of solar radiation, including visible light [16].

Table 2(a) Estimated bandgap of single SnGe

Single A-cation	
Mixture	**Estimate Bandgap (eV)**
$FASnGeI_3$	1.80
$CsSnGeI_3$	1.45
$MASnGeI_3$	1.60
$CsSnGeI_3$	1.45
$EASnGeI_3$	1.24
$CsSnGeI_3$	1.45

Table 2(b) Estimated bandgap of mixed SnGe

Mixed A-cation	
$AA'SnGeI_3$	**Estimate Bandgap (eV)**
FACs	1.63
$CsSnGeI_3$	1.45
MACs	1.53

4. CONCLUSION

In preliminary analysis, the crystal structure and optoelectronic characteristics of $EA_{0.5}Cs_{0.5}Sn_{0.5}Ge_{0.5}I_3$ are found to be almost cubic, with a tolerance factor of 0.99 and a bandgap lies within the SQ limit for Sn-based perovskite (1.34 eV). Nevertheless, experimental validation is essential for assessing the accuracy of proposed materials, verifying assumptions, identifying discrepancies, refining parameters and providing a robust foundation for further research and development.

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