



# Article Lead-Free and Stable Potassium Titanium Halide Perovskites: Synthesis, Characterization and Solar Cell Simulation

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**Abstract:** Titanium based double perovskites have shown good optical properties along with remarkable stability, making them promising lead-free perovskites for optoelectronic applications. In this work, Potassium Titanium Halide ( $K_2TiBr_6$ ,  $K_2TiI_6$  and  $K_2TiI_2Br_4$ ) double perovskites are synthesized for the first time. Surface topology and chemical composition are studied. Photoluminescence characterization shows a peak in the UV region. The perovskites exhibit quasi bandgap with  $K_2TiI_6$  having 1.62 eV direct bandgap, conducive for single junction solar cell fabrication.  $K_2TiBr_6$  and  $K_2TiI_2Br_4$  have bandgaps 2.14 eV and 2.44 eV, respectively, which is favorable for tandem solar cell application. The decomposition temperature of  $K_2TiI_6$  is notable at 678 °C, bestowing it with stability in ambient atmosphere. Inherent to its optical properties, Solar Cell Capacitance Simulator-1D (SCAPS-1D) is used to simulate perovskite solar cell (PSC) with  $K_2TiI_6$  as the absorber. Utilizing the absorption data from UV-Vis spectroscopy, these PSCs are designed to give maximum efficiency. Upon numerical optimization of perovskite layer thickness, we propose an efficient, practically realizable PSC with a power conversion efficiency of 4.382%. Besides, various electron and hole transport layers are investigated and the effect of their thickness on the PSC performance are studied.

Keywords: lead-free perovskites; inorganic and stable perovskites; photovoltaic cells; optoelectronics

#### 1. Introduction

The rapid development of the world's economy and productive forces are depleting conventional fossil fuel [1,2]. In recent times, numerous challenges, such as global crises of energy and resources, the environment, and climate change, has propelled the world towards the green industrial revolution. Renewable and cost-effective alternative energy resources including wind, thermal, solar, and hydro energy are proposed by scientists as the solution for these problems [3]. Solar energy has a strong lead among other resources, based on its abundance, cost-effectiveness, and environment friendliness. Photovoltaic (PV) technology contributes major part in harnessing solar energy. PV technology has undergone noteworthy evolution over the past few decades, including silicon-based solar cells, Si–Ge thin-film solar cells, dye-sensitized solar cells, quantum dot sensitized solar cells, and perovskite solar cells [4,5].

The creation of low-cost, high-efficiency solar cells has been the prominent issue in the recent years. Perovskite solar cells (PSCs), a promising class of solar cells family, has drawn a lot of attention in the last decade, due to their high absorption coefficient (e.g., CsSnI<sub>3</sub>), long carrier diffusion length (e.g., CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub>), low exciton binding energy (e.g., CsSnI<sub>3</sub>), low trap state density (e.g., CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub>), and tunable bandgap (e.g., CH<sub>3</sub>NH<sub>3</sub>Sn<sub>x</sub> Pb<sub>(1-x)</sub>I<sub>3</sub>) [6–11]. From the initial value of 3.8% to the most current value of 26.19%, the power conversion efficiency (PCE) of PSCs based on lead (Pb) perovskites has been significantly increased [12,13].

However, there are inherent drawbacks in these Pb-based high-efficiency PSCs (e.g., MAPbI<sub>3</sub>, FAPbI<sub>3</sub>,  $Cs_{0.05}FA_{0.85}MA_{0.10}Pb(I_{0.97}Br_{0.03})_3$ ), the foremost drawback being the



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). presence of lead, which is hazardous to organisms and the environment. Research shows that lead ion poisoning has a serious detrimental effect on the survival of people, animals, and plants [14,15]. Various degrees of lead poisoning have been studied, ranging from anemia, soft tissue damage to death in case of severe exposure [16–18]. Another notable problem is instability of Pb-based perovskites in the temperatures above 25 °C [19–21]. MAPbX<sub>3</sub> (X = I or Br) perovskites decomposed rapidly on constant exposure to light (100 suns for 60 min) at elevated temperatures around ~45 °C – ~ 55 °C. Consequently, to ensure that people's safety and pollution-free natural environment it is necessary to develop some non- or low-toxic metal ions to replace lead as perovskite absorbers in PSCs [22–24].

The universal chemical formula for metal halide perovskites is ABX<sub>3</sub>, where A is an organic cation, B is a metal cation, and X is a halogen anion [25,26]. The A cation in this case is usually methylammonium (MA), formamidinium (FA), Cs, or their mixture, and the halogen anion is normally Cl, Br, I, or their mixture. For B metal cation, previous research focused on less/non-toxic Sn<sup>2+</sup>, Bi<sup>3+</sup>, Ge<sup>2+</sup>, Sb<sup>3+</sup>, Mn<sup>2+</sup>, and Cu<sup>2+</sup>, as they have a similar electronic configuration to Pb [27,28]. The addition of these metal cations not only increases the diversity of perovskite species, but also improves PSCs' environmental friendliness. Unfortunately, most of them have low optical efficiency and less stability at ambient temperatures.

Titanium (Ti) based perovskites have lately been recommended as a promising alternative to Pb-free perovskites for solar cell applications [29]. Recent research on cesium titanium bromide  $Cs_2TiBr_6$  solar cell with conversion efficiency of 3.3%, paved the way for studies on this non-toxic alternative. Subsequent research on  $Cs_2TiCl/Br_6$ , proving them candidates for solar cells and other optoelectronic applications due to their high stability, non-toxic nature, visible band gap, and high conversion efficiency, piqued the interest of the scientific community [30,31]. The review by Ju et al. studied more Ti-based compounds, among which  $K_2TiX_6$  (X = I, Cl, Br) demonstrated huge potential for optical and thermoelectric device fabrication [29].  $K_2TiCl_6$  has been fabricated and studied extensively while,  $K_2TiI_6$ ,  $K_2TiBr_6$  are getting attention gradually. The non-toxic nature of  $K_2TiI_6$ ,  $K_2TiBr_6$  and  $K_2TiI_2Br_4$  has been more advantageous for commercial applications than the present inorganic  $Cs_2TiBr_6$ .

Motivated by previous theoretical works on  $K_2TiX_6$  (X = I, Br, Cl), this article uncovers the features of family of potassium titanium bromide iodide perovskites  $K_2TiI_6 K_2TiBr_6$ and  $K_2TiI_2Br_4$  for photovoltaic and optoelectronic application [32,33]. The perovskites are synthesized by low-cost solution method and the structural stability, electronic and optical properties of  $K_2TiI_6$ ,  $K_2TiBr_6$  and  $K_2TiI_2Br_4$  are studied. These materials have quasi-direct band gaps.  $K_2TiI_6$ ,  $K_2TiBr_6$  and  $K_2TiI_2Br_4$  have bandgaps in the increasing order of 1.62 eV, 2.14 eV, and 2.44 eV. Photoluminescence peaks are recorded at  $K_2TiI_6$  has bandgap closest to MAPbI<sub>3</sub>, the benchmark molecule that revolutionized PSCs. This perovskite also has high thermal stability, with decomposition temperature above ~670 °C. Owing to its bandgap and thermal stability, perovskite solar cell with  $K_2TiI_6$  absorber is simulated using Solar Cell Capacitance Simulator-1D (SCAPS-1D) with different Electron Transport Layers (ETLs) and Hole Transport Layers (HTLs) recording the highest PCE of 4.382%. Therefore, the comprehensive study of their optical and thermoelectric properties provides deep insight to researchers for the use of these materials commercially for energy applications.

#### 2. Materials and Methods

Potassium Titanium Bromide (K<sub>2</sub>TiBr<sub>6</sub>) powder was synthesized by the cost-effective 'solution method'. Potassium Bromide (KBr,  $\geq$ 99% trace metals basis, Sigma-Aldrich, St. Louis, MO, USA) powder was dissolved in water to form a saturated solution in which 1 mL of Hydro Bromic acid (HBr, 47% Avra, Telangana, India) was added. After the addition of acid, 2.3 g of Titanium (IV)Bromide (TiBr<sub>4</sub>, 98%, Alfa Aesar, Ward Hill, MA, USA) was added resulting in a brown solution. It was stirred at ~100 °C for 1 h to form residue. The pale-yellow residue (K<sub>2</sub>TiBr<sub>6</sub>) was collected after it was completely dried and ground to fine powder.

A similar process was employed to process  $K_2TiI_6$  and mixed halide  $K_2TiI_2Br_4$  powder. The ratio changes in the case of mixed halide perovskite, where  $TiI_4$  and  $TiBr_4$  were taken in the ratio 1:2 and added to aqueous solution containing KI and KBr in equal parts. Before the addition titanium halides, acids HI and HBr were added in small amounts. The mixture was then subject to heat and stirred till the water evaporated, before the residue was scraped and ground to form fine powder.

Powder X-ray diffraction (XRD) measurements were performed using a diffractometer (Bruker D8 Advance, Karlsruh, Germany) with Cu Ka radiation. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) images were collected using Carl Zeiss EVO18 SEM microscope (Oberkochen, Germany). The absorption spectra were captured using a Jasco V-670 ultraviolet-visible-near infrared (UV-Vis-NIR, Tokyo, Japan) spectrophotometer with an integrating sphere. Thermogravimetric analysis and differential temperature analysis (TGA and DTA) were performed using SDT Q600, (TA instruments, New Castle, DE, USA) scanning from 30 °C to 1000 °C, with a ramping rate of 20 °C/min. The photoluminescence spectra were measured using a Hitachi F-7000 FL spectrophotometer (Tokyo, Japan) excited by 150 W xenon lamp.

The Tauc method is employed to calculate direct and indirect bandgap from optical absorption spectra by the following equation:

$$(\alpha \cdot h\nu)^{1/\gamma} = B(h\nu - E_g)$$

where h is the Planck constant,  $\nu$  is the photon's frequency,  $E_g$  is the band gap energy, and *B* is a constant. The  $\gamma$  factor depends on the nature of the electron transition and is equal to 1/2 or 2 for the direct and indirect transition band gaps, respectively.

#### 3. Results and Discussion

### 3.1. Structural Analysis

XRD studies of K<sub>2</sub>TiBr<sub>6</sub>, K<sub>2</sub>TiI<sub>6</sub> and K<sub>2</sub>TiI<sub>2</sub>Br<sub>4</sub> perovskites are given below in Figure 1a. All three perovskites have face centered cubic structure with Fm3<sup>-</sup>m space group [32,33]. Based on the theoretical studies [32,33], the lattice constants of K<sub>2</sub>TiBr<sub>6</sub> and K<sub>2</sub>TiI<sub>6</sub> are 10.50 Å and 11.42 Å respectively. Values calculated from XRD pattern using Bragg's law for K<sub>2</sub>TiBr<sub>6</sub>, K<sub>2</sub>TiI<sub>6</sub> perovskites are a = 10.47 Å, 11.40 Å, agreeing closely to the theoretical values mentioned above. By Vegard's law, lattice constant of K<sub>2</sub>TiI<sub>2</sub>Br<sub>4</sub> is approximately a weighted mean of K<sub>2</sub>TiBr<sub>6</sub> and K<sub>2</sub>TiI<sub>6</sub>, hence a = 10.965 Å. Lattice parameters calculated from the XRD pattern have descending values in the order K<sub>2</sub>TiI<sub>6</sub> > K<sub>2</sub>TiI<sub>2</sub>Br<sub>4</sub> > K<sub>2</sub>TiBr<sub>6</sub>. This is justified by the increasing atomic radii of the halides. Lattice parameters are calculated by Bragg's law given below:

$$n\lambda = 2d \sin\Theta;$$

where the variable 'd' indicates the distance between the atomic layers, and the variable ' $\lambda$ ' specifies the wavelength of the incident X-ray beam and 'n' as an integer. ' $\Theta$ ' represents the angle of incidence.

The perovskites show structural stability as predicted by Goldschmidt tolerance factor values, which are as follows:  $K_2TiI_6 = 0.9026$  and  $K_2TiBr_6 = 0.9208$ . Despite the positive formation energy of  $K_2TiI_6$  [32], it is thermodynamically stable and has similar synthesis procedure compared to  $K_2TiBr_6$  and  $K_2TiI_2Br_4$ .

The perovskites were stored for a period of 10 months at room temperature. XRD of the samples after 10 months is shown in Figure 1b,  $K_2TiI_6$  shows change in peak intensity. Consequently, the FWHM of  $K_2TiI_6$  changes from 523.42° to 146.33°, thus altering the crystallite's size from 0.234 nm to 0.578 nm. FWHM stays the same for  $K_2TiBr_6$  (0.14° to 0.14°), whereas  $K_2TiI_2Br_4$  has slight difference from 0.23° to 1.17°. Change in crystallites size might be the contributing factor to intensity changes in  $K_2TiI_6$ . However, there is no shift in peak positions in all the three perovskites. There appears no change in  $K_2TiBr_6$  and  $K_2TiI_2Br_4$  pattern proving the stability of the perovskites. The physical appearance (i.e., the color, texture) of the powder sample remains the same even after this extended period. These perovskites are stable under light irradiation, providing a breakthrough in stable, lead-free alternative for lead based organic and inorganic perovskites.



Figure 1. XRD pattern of K<sub>2</sub>TiI<sub>6</sub>, K<sub>2</sub>TiI<sub>2</sub>Br<sub>4</sub> and K<sub>2</sub>TiBr<sub>6</sub> (a) when prepared (b) after 10 months.

Further analysis of structure was carried out using SEM and EDX. Figure 2a,d represents SEM images and chemical composition of  $K_2TiI_6$ . It showed clusters made up of cube like grains. Figure 2b,e is the SEM and EDX of  $K_2TiBr_6$ , exhibiting irregular shaped structure which shows cubic grains on closer magnification. Figure 2c,f denotes the SEM and EDX spectrum of mixed halide perovskite  $K_2TiI_2Br_4$ , which exhibits irregular, angular shaped flaky grains. A closer look at the SEM images shows non-porous grains, contrary to their cesium-based counterpart formed by the same method [31]. In addition, these perovskites are soluble in water. This quality opens many avenues for easy deposition process, in turn greatly helping to realize efficient thin film devices.



**Figure 2.** SEM images of (a)  $K_2 TiI_6$ ; (b) SEM of  $K_2 TiBr_6$ ; (c) SEM image of  $K_2 TiI_2 Br_4$ . (d) EDX spectrum of  $K_2 TiI_6$  (e) EDX spectrum of  $K_2 TiBr_6$  (f) EDX spectrum of  $K_2 TiI_2 Br_4$ .

The elemental composition of all three perovskites as found by EDAX is given in Table 1. No contamination or moisture is detected in the perovskites.

Element (K <sub>2</sub> TiBr <sub>6</sub> )	Weight%	Atomic%	Element (K <sub>2</sub> TiI <sub>6</sub> )	Weight %	Atomic%	Element (K <sub>2</sub> TiI <sub>2</sub> Br <sub>4</sub> )	Weight%	Atomic%
К К	18.65	26.37	К К	24.50	43.83	K <i>K</i>	21.11	34.96
Ti K	37.49	43.28	Ti K	16.01	23.38	Ti K	12.86	17.39
Br L	43.86	30.35	I L	59.49	32.79	Br L	46.49	37.68
						I L	19.54	9.97
Total	100.00		Total	100.00		Total	100.00	

Table 1. Energy dispersive X-ray analysis of K<sub>2</sub>TiI<sub>6</sub>, K<sub>2</sub>TiBr<sub>6</sub> and K<sub>2</sub>TiI<sub>2</sub>Br<sub>4</sub>.

# 3.2. Optoelectronic Properties

The perovskites were characterized to find their optical properties. Absorbance curves of  $K_2TiI_6$ ,  $K_2TiBr_6$  and  $K_2TiI_2Br_4$  are given in Figure 3.  $K_2TiBr_6$  has high absorbance in the ultraviolet (UV) region with a peak at 327 nm,  $K_2TiI_6$  and  $K_2TiI_2Br_4$  have high absorbance in the UV region with peak absorbance at 301 nm and 300 nm, respectively.



Figure 3. Absorption curve for K<sub>2</sub>TiI<sub>6</sub>, K<sub>2</sub>TiBr<sub>6</sub> and K<sub>2</sub>TiI<sub>2</sub>Br<sub>4</sub>.

Absorbance in the visible region of the solar spectrum is desired for photovoltaic applications. While UV radiation makes around 4–8% of solar spectrum, they have longer wavelength, consequently having high energy per photon. UV photons have been reported to damage the perovskite solar cells, on exposure for a certain period. To minimize the damage caused by UV radiation, UV filtering, e.g., luminescent down shifting (LDS), can be used to preserve the solar cells [34].

Bandgaps for the perovskites are calculated by Tauc plots (Figure 4).  $K_2TiI_6$  has direct bandgap of 1.62 eV and  $K_2TiBr_6$  has direct bandgap of 2.14 eV (Figure 4a). Indirect bandgaps of  $K_2TiI_6$ ,  $K_2TiBr_6$  are 1.50 eV and 1.54 eV respectively as given in Figure 4b. The samples have quasi-direct bandgaps, since the difference between direct and indirect bandgap is very small (<30 meV). These values are in accordance with the theoretical studies published in various research articles [32,33]. The distinct difference in bandgaps of  $K_2TiI_6$  and  $K_2TiBr_6$ is due to Halide atom p- orbitals dominating VBM, while Ti-3d orbitals dominate CBM. The effect of halide atom ionic radius variation affects the CBM edges, and it increases the bandgap from Br to I. The 4 s orbitals of K contribute nothing to the VBM and CBM edges [32]. Direct bandgap of  $K_2TiI_6$  is conducive to be an absorber in single junction solar cell. Large bandgap perovskite  $K_2TiBr_6$  can be employed in multi-junction solar cell, in tandem with low bandgap absorbers like silicon [35,36].  $K_2TiI_2Br_4$  has the direct bandgap of 2.44 eV (Figure 4a) and  $K_2TiI_4Br_2$  has bandgap 2.30 eV as represented in Figure 4c. Indirect bandgap of  $K_2TiI_2Br_4$  and  $K_2TiI_4Br_2$  are 1.58 eV and 1.59 eV respectively (Figure 4d). Here,  $K_2TiI_2Br_4$  has a larger bandgap compared to  $K_2TiI_4Br_2$ . Evidently, mixed halide perovskites have wide bandgap which can be tuned easily by changing the chemical composition of halides.



**Figure 4.** Tauc plot for (**a**) direct bandgap of K<sub>2</sub>TiBr<sub>6</sub>, K<sub>2</sub>TiI<sub>6</sub> and K<sub>2</sub>TiI<sub>2</sub>Br<sub>4</sub> and (**b**) indirect bandgap of K<sub>2</sub>TiBr<sub>6</sub>, K<sub>2</sub>TiI<sub>6</sub> and K<sub>2</sub>TiI<sub>2</sub>Br<sub>4</sub>. (**c**) Direct bandgap of K<sub>2</sub>TiI<sub>4</sub>Br<sub>2</sub> and (**d**) indirect bandgap of K<sub>2</sub>TiI<sub>4</sub>Br<sub>2</sub>.

Photoluminescence spectroscopy results are shown in Figure 5. Emission peaks are in the visible region and red shifted in the order  $K_2TiI_2Br_4 < K_2TiBr_6 < K_2TiI_6$ . PL intensity of mixed halide perovskite is less compared to bromide and iodide perovskites. Transition bandgap calculated from Figure 5 is similar to the bandgap intercepted from Tauc plot. This shows low defect density in all these perovskites. The FWHM of  $K_2TiI_6$  is 7.15 nm, while  $K_2TiBr_6$  and  $K_2TiI_2Br_4$  have values 1.06 nm and 16.76 nm respectively. PL spectra of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> recorded broad high intensity peak at ~786 nm corresponding to its reported bandgap value (~1.60 eV) [37].



Figure 5. PL spectra of K<sub>2</sub>TiI<sub>2</sub>Br<sub>4</sub>, K<sub>2</sub>TiBr<sub>6</sub>, and K<sub>2</sub>TiI<sub>6</sub>.

Since the bandgap of  $K_2 TiI_6$  is closer to the organic and most efficient  $CH_3NH_3PbI_3$ perovskite, it is extensively studied below [38,39]. For an efficient photovoltaic device application, PL studies on individual layers that constitute the cell can provide important information on carrier recombination and charge extraction from absorber layer. Specifically, observing the variation in PL intensity under continuous excitation, provides the knowledge about device stability and optimization [40]. To further explore this perovskite, its thermal stability is studied and SCAPS-1D is employed to give a suitable solar cell assembly to obtain maximum power conversion efficiency.

#### 3.3. Thermal Stability

Thermal stability of perovskites is found using TGA. Figure 6a represents TG analysis of  $K_2$ TiI<sub>6</sub>. The decomposition temperature is high at 678.36 °C, which makes it stable under high temperature conditions. Figure 6b compares the DTA curve of  $K_2$ TiI<sub>6</sub> and KI.  $K_2$ TiI<sub>6</sub> shows endothermic behavior till 157 °C, decomposition happens at 681 °C into KI and TiI<sub>4</sub>, and then proceeds to decompose completely at 880 °C.



Figure 6. (a) Thermogravimetric analysis of  $K_2 TiI_6$ ; (b) Differential thermal analysis of  $K_2 TiI_6$  and KI.

Weight loss of the sample is very less till 678.36 °C, showing the absence of moisture.  $K_2 TiI_6$  displays high thermal stability compared to other Ti-based perovskites [31]. This property makes it promising for photovoltaic application in elevated temperature conditions.

#### 4. Solar Cell Simulation

One-dimensional solar cell capacitance simulator SCAPS (version 3.3.10) as a simulation platform is employed to study the application of the perovskites in solar cell devices [41,42]. This software is a general solar cell simulator program that can be used in the simulation, numerical analysis, and tracking the behavior of the photovoltaic structure. The software is mainly based on solving continuity, Poisson, and semi-conductor equations to describe the physics of the photovoltaic structure.

The three perovskites showed remarkable optoelectronic properties. However,  $K_2TiI_6$  has bandgap value very close to that of  $CH_3NH_3PbI_3$  (~1.60 eV). And  $CH_3NH_3PbI_3$  has high power conversion efficiency with practical efficiency limit up to 29.53% [43]. Since they have similar optical properties, the bandgap of  $K_2TiI_6$  is considered optimal and the solar cell devices based on it will have high efficiency.

SCAPS-1D is used to simulate a single-junction solar cell with the inorganic  $K_2 TiI_6$  as absorber, using the absorbance data from the sample processed earlier. Since the absorbance data for the material from experiment are applied, the chances of getting accurate results are high, which will help in fabricating the right device. The parameters used for simulation are given below in Table 2.

Parameters	FTO	ZnO	TiO <sub>2</sub>	K <sub>2</sub> TiI <sub>6</sub>	PEDOT: PSS	РЗНТ
Eg (eV)	3.5	3.3	3.2	1.61	2.2	2
χ (eV)	4.4	4.1	4.1	4	2.9	3.2
ε <sub>r</sub>	9	9	9	10	3	3
$N_{c} (cm^{-3})$	$2.2  imes 10^{18}$	$4 imes 10^{18}$	$1  imes 10^{21}$	$1 imes 10^{19}$	$2.2 imes10^{15}$	$1  imes 10^{20}$
$N_v (cm^{-3})$	$1.8 imes10^{19}$	$1  imes 10^{19}$	$2  imes 10^{20}$	$1 imes 10^{19}$	$1.8 imes10^{18}$	$1 \times 10^{20}$
$\mu_n$ (cm <sup>2</sup> /Vs)	20	200	20	4.4	10	0.0001
$\mu_p (cm^2/Vs)$	10	25	10	2.5	10	0.0001
$N_{\rm D}  ({\rm cm}^{-3})$	$1  imes 10^{19}$	$1  imes 10^{18}$	$1  imes 10^{19}$	$3 imes 10^{19}$	0	0
$N_{\rm A}~({\rm cm}^{-3})$	0	0	0	$3 imes 10^{18}$	$3.17 imes10^{14}$	$1  imes 10^{16}$
Ref.	[44]	[45,46]	[45,46]	[32,33]	[47,48]	[49]

**Table 2.** Parameters used in simulation of K<sub>2</sub>TiI<sub>6</sub> based PSC.

Parameters for  $K_2 TiI_6$  are from experiment carried out and from computational studies by various researchers. Two different electron transport layers (ETLs) and a Hole Transport Layer (HTL) are chosen [44–49] to optimize device configuration, for obtaining maximum efficiency. TiO<sub>2</sub> and ZnO are the most widely used ETL, whose wide bandgap helps with higher extraction and transportation of electrons from perovskite layer to ETL. Commonly used HTL poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) and Poly(3-hexylthiophene) (P3HT), possessing high hole mobility and stability are employed to study the performance of the perovskite K<sub>2</sub>TiI<sub>6</sub> as absorber. Significant qualities, such as the low cost and easy deposition process, of these transport layers are highly desired over widely used HTL (Spiro-MeOTAD) and ETL (SnO<sub>2</sub>). The following are the four devices: Device 1- FTO/TiO<sub>2</sub>/K<sub>2</sub>TiI<sub>6</sub>/PEDOT: PSS/Metal contact, Device 2-FTO/ZnO/K<sub>2</sub>TiI<sub>6</sub>/PEDOT: PSS/Metal contact, Device 3- FTO/TiO<sub>2</sub>/K<sub>2</sub>TiI<sub>6</sub>/P3HT/Metal contact and Device 4-FTO/ZnO/K<sub>2</sub>TiI<sub>6</sub>/P3HT/Metal contact, to be studied in detail, and represented schematically in Figure 7. With the inclusion of defect density to all the layers, the results are obtained as shown below.

<b>Device 1</b>	Device 2	Device 3	<b>Device 4</b>
Metal contact	Metal contact	Metal contact	Metal contact
PEDOT:PSS	PEDOT:PSS	РЗНТ	РЗНТ
K <sub>2</sub> Til <sub>6</sub>	K <sub>2</sub> Til <sub>6</sub>	K <sub>2</sub> Til <sub>6</sub>	K <sub>2</sub> TiI <sub>6</sub>
TiO <sub>2</sub>	ZnO	TiO <sub>2</sub>	ZnO
FTO	FTO	FTO	FTO

Figure 7. Schematic representation of solar cell devices.

#### 4.1. Effect of Absorber Layer Thickness

The PSCs are studied by changing their absorber layer thickness, while the electron and hole transport layers width were constant. To optimize the absorber width of the devices, the thickness of FTO conductive glass is fixed at 150 nm throughout the simulation. The thickness of ETLs  $TiO_2$  and ZnO are fixed at 400 nm and 500 nm respectively. HTLs PEDOT:PSS and P3HT are set as 400 nm and 50 nm respectively.

 $K_2$ TiI<sub>6</sub> layer was varied from 200 nm to 1000 nm, and their current density vs. Voltage behavior is observed. Figure 8 represents the current density vs. voltage graph of all the devices for 200 nm absorber thickness. Variation of  $K_2$ TiI<sub>6</sub> thickness from 200 nm to 1000 nm has no notable effect on the current density vs. voltage relation.



**Figure 8.** Current density versus voltage plot for 200 nm thickness of absorber layer in the devices 1, 2, 3 and 4.

For all the devices, open circuit voltage ( $V_{oc}$ ), short circuit current ( $J_{sc}$ ), and power conversion efficiency (PCE) decreases with increase in thickness. Fill factor keeps increasing with thickness (Figure 9). The charge carriers have a longer route with thicker absorber layer, which decreases the carrier collection at the electrodes, and the increase of carrier recombination results in decrease of  $V_{oc}$ ,  $J_{sc}$  and PCE [50]. The increase of series resistance with a thicker absorber layer shows an increasing trend in *FF* [51]. Hence, the 200-nm thick absorber layer is chosen for optimum performance of the PSC with various electron and hole transport layers. Table 3 presents the comparative analysis of cell parameters for all the devices studied at favorable thickness of absorber and transport layers.



Figure 9. Voc, Jsc, fill factor and PCE of devices 1, 2, 3 and 4 for different absorber layer thickness.

Device	Configuration	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF %	PCE %
1	FTO/TiO <sub>2</sub> /K <sub>2</sub> TiI <sub>6</sub> /PEDOT: PSS	1.1557	7.8647	47.9585	4.3593
2	FTO/ZnO/K <sub>2</sub> TiI <sub>6</sub> /PEDOT: PSS	0.9450	5.3580	45.9063	2.3245
3	FTO/TiO <sub>2</sub> /K <sub>2</sub> TiI <sub>6</sub> /P3HT	1.0003	2.2905	45.5032	1.0428
4	FTO/ZnO/K <sub>2</sub> TiI <sub>6</sub> /P3HT	1.0701	2.6554	51.2958	1.4576

Table 3. Comparative analysis of cell parameters for K<sub>2</sub>TiI<sub>6</sub> based PSCs.

# 4.2. Performance of PSC with Varying ETL Thickness

Electron transport layers are essential in providing various functions like, charge transfer and preventing charge recombination. The most common and efficient inorganic ETLs- Titanium dioxide (TiO<sub>2</sub>) and Zinc oxide (ZnO), are employed in these devices, whose width is varied from 100–500 nm, while keeping the HTLs (PEDOT: PSS) and P3HT thickness unchanged to optimize these PSC devices. With the thickness of FTO and  $K_2$ TiI<sub>6</sub> fixed at 150 nm and 200 nm respectively, ETL layers' thicknesses are varied to optimize the devices. Figure 10 shows the V<sub>oc</sub>, J<sub>sc</sub>, Fill factor and PCE curve for varying ETL thickness. Increase in the thickness of ETLs shows increase in V<sub>oc</sub>, J<sub>sc</sub> and PCE, while FF decreases. Devices 1 and 3 registered the highest efficiency for TiO<sub>2</sub> thickness of 400 nm. In the case of devices 2 and 4, ZnO thickness maintained up to 500 nm to get the highest possible output.



Figure 10. Comparing the values of Voc, Jsc, Fill factor and PCE for varying ETL thickness.

#### 4.3. Performance of PSC with Different HTL Thickness

The variation of the simulated parameters as a function of the thickness of the p-layer in the range from 10 nm to 400 nm is displayed in Figure 11 where the thickness values for the ET layer and absorber layer are set at their optimal values of 400 nm and 200 nm, respectively for devices 1 and 3. Two other devices with ZnO ETL (devices 3 and 4), were fixed the values 500 nm and 200 nm for ETL and absorber layer as thickness to study the effect of HTLs. Polymers poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and Poly(3-hexylthiophene) (P3HT) as HTL are simulated. Multiple tries were made to optimize the device. It is observed that the thickness of P3HT has direct effect on the device performance. For higher P3HT layer width (>40 nm), the device registered less PCE. Optimized device thickness for best efficiency is TiO<sub>2</sub>-400 nm, ZnO-500 nm; K<sub>2</sub>TiI<sub>6</sub>—200 nm and P3HT—40 nm. For the same transport layer thickness, the absorber layer width was varied which reduced the device efficiency. Device 3 had the configuration FTO/TiO<sub>2</sub>/K<sub>2</sub>TiI<sub>6</sub>/P3HT, which recorded the maximum power conversion efficiency of 1.0428%.



**Figure 11.** Values of  $V_{oc}$ ,  $J_{sc}$ , FF and PCE for varying thickness of HTL with fixed thickness of ETL and  $K_2 TiI_6$ .

Device 1 and 2 demonstrated distinct behavior with different thicknesses of PE-DOT:PSS. The optimal width of PEDOT:PSS is 400 nm for device 1 and 200 nm for device 2. These devices showed maximum efficiency for larger thickness compared to P3HT devices. Figure 11 compares the different parameters  $V_{oc}$ ,  $J_{sc}$ , FF, PCE for devices 1, 2, 3 and 4.

# 5. Conclusions

In this article, inorganic vacancy ordered double perovskites  $K_2TiI_6$ ,  $K_2TiB_6$  and  $K_2TiI_2Br_4$  are processed by a low-cost solution method [31] and subsequently characterized. Owing to the Goldschmidt tolerance factor, XRD studies confirm that potassium titanium halides perovskites exhibit single phase crystalline nature. On further structural characterization, SEM studies showed cube shaped grains, while EDAX gave an account of the chemical composition of the perovskites. In order to determine the optical properties, UV-Vis spectroscopy was employed. Absorption spectra shows absorbance in the UV region for all the three perovskites. To minimize the effect of UV photons degrading the perovskites on prolonged exposure, luminescent down shifting is recommended. The optical bandgap intercepted from Tauc plot shows all the three perovskites  $K_2TiI_6$ ,  $K_2TiBr_6$  and

 $K_2TiI_2Br_4$  have quasi bandgaps.  $K_2TiI_6$  has the desirable direct bandgap of 1.62 eV,  $K_2TiBr_6$ has direct bandgap of 2.2 eV and K<sub>2</sub>Til<sub>2</sub>Br<sub>4</sub> has direct bandgap of 2.44 eV. The optical gap of Potassium Titanium Iodide is narrow like the most successful organic perovskite, Methylammonium Lead Iodide (MAPbI<sub>3</sub>), proving to be a promising candidate for lead-free, low-cost perovskite. K<sub>2</sub>TiBr<sub>6</sub> and K<sub>2</sub>TiI<sub>2</sub>Br<sub>4</sub> can help in realizing efficient tandem devices with CdTe, silicon, and CIGS. Narrow bandgap of CdTe, CIGS and silicon has proved to be more efficient in tandem with perovskites with optical gap larger than 2 eV [49,50]. As  $K_2$ TiI<sub>6</sub> perovskite appears more suitable for absorber in single junction solar cell, we check its thermal stability by TGA and DTA. With 678.36 °C decomposition temperature, it shows remarkable thermal stability. Based on its various merits, SCAPS-1D is used to simulate K<sub>2</sub>TiI<sub>6</sub> based solar cells with the help of absorption data obtained from UV-Vis spectroscopy. By varying ETLs and HTLs, the device is optimized to attain maximum efficiency. The solar cell device with following configuration  $FTO/ZnO/K_2TiI_6/PEDOT$ : PSS showed maximum power conversion efficiency of 4.3821%. To conclude, Potassium Titanium Halides are synthesized and characterized, based on the results obtained using two sets of  $K_2TiI_6$  perovskite solar cells simulated using SCAPS-1D, providing a promising solution for lead-free, cost effective, bio-friendly, thermally stable, and efficient perovskite.

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