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KBaTeBiO₆: a lead-free, inorganic double-perovskite semiconductor for photovoltaic applications

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3 **KBaTeBiO₆: a lead-free, inorganic double-perovskite semiconductor**
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6 **for photovoltaic applications**
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Abstract:

Solar cells made up of lead-halide perovskites have shown a remarkable increase in power conversion efficiency; however, they are plagued with instability issues that combined with the toxicity of lead have led to a search for new semiconductors made up of heavy and non-toxic metals such as bismuth. Here, we report on a new, inorganic, double perovskite oxide semiconductor: KBaTeBiO_6 , which has an experimental indirect band gap of 1.88 eV and shows excellent stability. We combined data analytics and high throughput density-functional-theory calculations to search through thousands of hypothetical inorganic double perovskite oxides containing bismuth and predict KBaTeBiO_6 as a potential photovoltaic material, which was subsequently synthesized using a wet-chemistry route. The calculated effective mass of the charge carriers for KBaTeBiO_6 is comparable to the best performing Bi-halide double perovskites. Our work demonstrates the untapped potential of inorganic Bi-based double perovskite oxides—that offer the ability to change both the cation combination and their stoichiometry to achieve desired electronic properties—as exciting, benign and stable alternatives to lead-halide perovskites for various semiconducting applications.

Introduction:

Lead-halide perovskites have been an area of extensive research since the observation of photovoltaic effect in $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ in 2009.¹ The power conversion efficiency of these perovskites has now reached 22.7%;² however, they show poor stability and degraded performance on exposure to sunlight and moisture.³⁻⁵ While effective encapsulation methods and processing routes, such as electrospray deposition have demonstrated enhanced stability, change to a more stable composition is still desirable.⁶ Additionally, the use of lead, a toxic element, raises questions of potential toxicity.⁷ Therefore, there is an ongoing search to find stable and environmentally benign alternatives to lead-halide perovskites. The substitution of lead with lighter group IV cations, such as Sn and Ge, has yielded limited success due to the instability of +2 oxidation state in these cations.⁸⁻⁹ The heavy Pb^{2+} cation with its occupied $6s^2$ lone-pair electrons is pivotal to attain an electronic structure that facilitates efficient charge collection and makes them optimal for solar cell applications.¹⁰ The delocalized nature of the Pb $6p$ states leads to a highly dispersed conduction band with a low effective mass of the electrons. The valence band edge is formed of antibonding states of Pb $6s^2$ hybridized with the p -states of the halide anions, which reduces the effective mass of the holes. Moreover, the presence of antibonding states at the valence band edge results in defect levels that are either shallow or lie within the bands.¹¹ The Pb $6s^2$ lone-pair electrons also result in a large dielectric constant that improves carrier lifetimes by effectively screening charged defects and by reducing the exciton binding energies.¹² Overall, the combination of a large dielectric constant and the presence of antibonding states at the valence band edge have been attributed to the remarkable defect-tolerance that these lead-halide perovskites exhibit.¹¹⁻¹⁵

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3 It is attractive to replace Pb^{2+} with an isoelectronic and non-toxic cation such as Bi^{3+} . Many
4 of the bismuth-halide semiconductors proposed recently for photovoltaic applications have a
5 layered structure with broken Bi_6X_6 octahedral connectivity along one or more crystallographic
6 directions, which results in flat electronic bands.¹⁶⁻¹⁸ To improve the dispersion of the bands, a
7 three-dimensional (3D) connectivity of the Bi_6X_6 octahedra,¹⁹ as observed in the perovskite
8 structure, is required; however, due to charge neutrality reasons, it is not possible to obtain defect-
9 free halide perovskites with a Bi^{3+} cation. Recently, double perovskite halides with a stoichiometry
10 of $A_2\text{B}\text{Bi}_6\text{X}_6$, where A is a larger monovalent cation, B is a smaller monovalent cation that
11 alternatively occupies the octahedral site with Bi, and X is a halide ion have been proposed as
12 potential alternatives.²⁰⁻²⁴ Examples include $\text{Cs}_2\text{AgBiBr}_6$,²¹⁻²² $\text{Cs}_2\text{AgBiCl}_6$,²² and
13 $(\text{CH}_3\text{NH}_3)_2\text{AgBiBr}_6$.²⁴ These double perovskite halides have highly dispersed valence and
14 conduction bands²² and show large carrier lifetimes comparable to lead-halide perovskites.²¹
15 However, all the reported $A\text{B}\text{Bi}_6\text{X}_6$ double perovskites have an indirect band gap that in most cases
16 is within 2 – 3 eV, which restricts efficient utilization of the solar spectrum. Of the reported
17 compounds, $\text{Cs}_2\text{AgBiBr}_6$ is most promising having an indirect band gap of 1.95 eV.²¹⁻²²
18 Furthermore, these compounds are observed to degrade over a period of few weeks on exposure
19 to ambient air and light with the degradation being more severe for $\text{Cs}_2\text{AgBiBr}_6$.²² Finally, the use
20 of monovalent halides restricts the composition space for combining different A and B cations to
21 achieve the desired properties.²⁰

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24 To overcome the above challenges and achieve stable compounds containing Bi^{3+} cations
25 within a 3D-octahedral framework having a low band gap suitable for photovoltaic applications,
26 we have explored the family of double perovskite oxides with a general stoichiometry of
27 $A'\text{A}''\text{B}'\text{BiO}_6$. Based on charge neutrality conditions, one can obtain a vast composition space of
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3 29,515 unique $A'A''B'BiO_6$ double perovskites. Previously, cation substitution has been
4 demonstrated to vary the band gap in oxide perovskites from 1.1 – 3.8 eV,²⁵⁻²⁶ which indicates the
5 possibility to obtain low band gap $A'A''B'BiO_6$ double perovskites. However, a search of the
6 inorganic crystal structure database (ICSD)²⁷ for $A'A''B'BiO_6$ leads to only 28 unique compounds,
7 with a nearly equal stoichiometry of all the four cations. To rapidly discover stable promising
8 compounds from the vast composition space, we have used a combination of high-throughput
9 density-functional-theory (DFT) calculations and data analytics. We have used a linear regression
10 model based on the octahedral (o) and tolerance factors (t) of the experimentally observed
11 $A'A''B'BiO_6$ compounds to screen hypothetical compounds that are expected to be stable.
12 Subsequently, we have used DFT calculations to identify thermodynamically stable $A'A''B'BiO_6$
13 compounds and their electronic structure. Of the several new $A'A''B'BiO_6$ compounds that we find
14 to be theoretically stable, we predict $KBaTeBiO_6$ to have an indirect theoretical band gap of 1.94
15 eV with highly dispersed conduction and valence bands. The predicted band gap and effective
16 masses of the charge carriers in $KBaTeBiO_6$ are comparable to $Cs_2AgBiBr_6$. Finally, we have
17 synthesized $KBaTeBiO_6$ nanoparticles using a wet chemistry approach, which shows excellent
18 stability for over a year under ambient conditions (no glove box). We confirm the formation of a
19 perovskite phase for $KBaTeBiO_6$ using X-ray powder diffraction (XRD) and aberration-corrected
20 scanning transmission electron microscopy (STEM). We obtain an experimental indirect band gap
21 of 1.88 eV, in good agreement with the theoretical predictions. Finally, we have fabricated
22 photoelectrochemical (PEC) solar cell devices using $KBaTeBiO_6$ nanoparticles. These first-
23 generation solar cells, that have not been optimized, show an average efficiency of 0.04 %. Overall,
24 our work opens a vast new composition space of environmentally benign bismuth-oxide
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3 perovskites that offer large tunability of their optoelectronic properties to obtain high-performance
4 semiconductors for various applications.
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8 **Methods:**
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11 **Computational Details:** DFT calculations were performed using the Vienna Ab-initio Simulation
12 Package (VASP)²⁸ using the projector-augmented-wave (PAW) method.²⁹ We employed
13 generalized gradient approximation (GGA) as implemented in the Perdew-Burke-Ernzerhof (PBE)
14 functional³⁰ for crystal and electronic structure optimization. The enforcement of layered and rock-
15 salt ordering at the *A* and *B*-site, respectively, lead to a 20-atom supercell having two formula units
16 (f.u.) of the double perovskite. This supercell is a $\sqrt{2} \times \sqrt{2} \times 2$ transformation of a typical 5-atom
17 ABX_3 perovskite primitive unit cell. The initial lattice parameters for geometric optimization (*a*, *b*
18 and *c*) were approximated from the Slater's atomic radii such that $a = b = 2\sqrt{2}(r_B + r_X)$ and
19 $c = 4(r_B + r_X)$. We used a plane-wave basis set with a cutoff energy of 400 eV for the coarse and
20 fine relaxation steps, and 520 eV for the final static total energy calculation step. The Brillouin
21 zone was sampled using a Gamma-centered Monkhorst-Pack³¹ *k*-points mesh while keeping the *k*-
22 points per reciprocal atom (KPPRA) ~8000 for the fine relaxation and the single-step static
23 calculation. The fine relaxation and the static calculation were carried out in accordance with
24 pseudopotentials and other DFT settings employed by OQMD.³² For the HSE06 calculations, the
25 fraction of Hartree-Fock exchange (α) was fixed at 0.25, and an inverse screening length of 0.207
26 Å⁻¹ was used.
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30 **Synthesis and characterization:** KBaTeBiO₆ was synthesized using a simple wet-chemistry
31 route. KNO₃ (Fisher Scientific, USA), Ba(NO₃)₂ (Sigma Aldrich, USA), Te(OH)₆ (Sigma Aldrich,
32 USA), and Bi(NO₃)₃.5H₂O (Alfa Aesar, USA) were used as the precursors for each element. A
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3 solution of each precursor was prepared separately in deionized water, except for $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$,
4 which was prepared in HNO_3 and water mixture (1:3 ratio of $\text{HNO}_3:\text{H}_2\text{O}$). An equimolar mixture
5 solution with 0.1 M concentration of these precursors was then prepared in nitric acid. The
6 precursor mixture was dried overnight (12 hours) in a muffle furnace at 100 °C. After complete
7 drying, the dried precursor powder (0.31 g in one batch) was annealed at 650 °C for 6 hours (time
8 after reaching the desired temperature). Thermogravimetric and differential thermal analyses
9 (TGA/DTA) (TA Instruments, New Castle, DE) was performed to choose a proper temperature
10 for annealing based on the decomposition profile of the precursors. The annealed powders were
11 characterized to investigate crystal structure, optical properties (band gap) and elemental
12 composition. Crystal structure information was obtained using an X-ray diffractometer (XRD,
13 Bruker D8 Advance, Bruker, USA) in Bragg–Brentano geometry, configured with a 1.5418 Å Cu
14 X-ray under an operating condition of 40 kV. Analysis of the XRD pattern and peak search was
15 performed using the DIFFRACTION.SUITE Eva software. The absorption and reflection spectra
16 of the double perovskite (thin film on a glass slide) were measured using a UV-vis
17 spectrophotometer (UV-2600, Shimadzu, USA) with an integrating sphere (ISR-2600 Plus,
18 Shimadzu, USA) over 300-900 nm with a step size of 0.5 nm. Elemental composition was
19 determined using scanning transmission electron microscope (STEM; JEOL 2200FS) Field-
20 Emission STEM/TEM instrument equipped with a CEOS GmbH (Heidelberg, Ger) corrector
21 operated at an acceleration voltage of 200 kV. The microscope is equipped with a Bruker-AXS
22 silicon-drift detector system (SDD) to utilize energy dispersive X-ray spectroscopy (EDS) methods
23 such as elemental mapping. The elemental X-ray hypermaps were acquired with a nominal beam
24 current of 200 pA to optimize the count rate for acquisition. The sample was prepared using
25 KBaTeBiO_6 in hexane solution on lacey carbon films on copper TEM grids.
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The atomic resolution STEM imaging was carried out at Oak Ridge National Laboratory using the aberration-corrected Nion UltraSTEM™ 200 microscope operated at 200 kV, which is equipped with a fifth-order aberration corrector and a cold field-emission electron gun. KBaTeBiO₆ powder was dispersed on a lacey carbon TEM grid using dip-casting. The TEM grids were heated to 160 °C in vacuum to remove excess solvent and contamination. To accurately determine the atomic positions of atomic columns in HAADF images, Gaussian blurring was used to smooth out the HAADF images.

Fabrication of photoelectrochemical solar cells: KBaTeBiO₆ powder was used to prepare KBaTeBiO₆ solution by two methods. In the first method, KBaTeBiO₆ powder was mixed with ethanol and water in a ratio of 2:1 followed by a few minutes of sonication and stirring. In the second method, KBaTeBiO₆ solution was prepared following a previously reported method,³³⁻³⁴ where acetic acid, water, and ethanol were added dropwise to the obtained powder and were ground well with mortar and pestle for approximately 30 minutes. Then, terpineol and ethyl cellulose solution in ethanol (5%) were added as binders. The mixture was again ground well and transferred to a vial with excess ethanol for a few minutes of stirring and sonication.

For the device fabrication, the KBaTeBiO₆ solution was drop casted on a TiO₂ opaque electrode (Solaronix, Australia), which consists of TiO₂ nanoparticles (15-20 nm and >100 nm), which consists of a screen printed active transparent layer of Ti-Nanoxide covered by a reflective layer of Ti-Nanoxide resulting in an overall TiO₂ layer thickness between 12-16 µm. The TiO₂ film was then annealed at 450 °C for 30 min before coating the KBaTeBiO₆ layer. The KBaTeBiO₆ solution was drop-casted on the TiO₂ electrode followed by annealing at 100 °C for 15 min for the first solution and 400 °C for 30 min for the second KBaTeBiO₆ solution. The higher annealing temperature for the second solution is required to remove the binders. KBaTeBiO₆ coated

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3 TiO₂/FTO electrode acts as a working electrode and a Pt electrode was used as the counter
4 electrode. The two electrodes were then sandwiched together with 25 μ m thick thermoplastic
5 surlyn film and the iodide/triiodide electrolyte (iodolyte AN-50, Solaronix) was injected between
6 the electrodes through a pre-drilled hole on the Pt electrode (Solaronix, Australia), which is made
7 from screen-printing a Platisol T/SP precursor on FTO substrate. The active area of the cells was
8 0.25 cm². All the devices were tested under the standard AM1.5 solar illumination conditions. The
9 entire device fabrication and testing were performed under ambient humid conditions (30-50 %
10 relative humidity). No glove box was used during material synthesis and device testing.
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Results and discussion:

An ideal double perovskite with a general formula of $A'A''B'B''X_6$ is an extension of the cubic ABX_3 perovskite structure, where A' and A'' represent inequivalent A -site cations while B' and B'' represent inequivalent B -site cations. The B -site cations are octahedrally (6-coordinated) coordinated by the X -site anions, while the A -site cations occupy the cubo-octahedral (12-coordinated) voids generated within the rigid, corner-connected BX_6 octahedral network, as shown in Figure 1a. For a fixed anion X , the perovskite structure can accommodate a varied range of cations both at the A and B -sites.³⁵ This flexibility arises from the ability of the BX_6 octahedra to undergo cooperative tiltings³⁶ that optimize the coordination environment of the cations. In our search for inorganic oxide double perovskites that can mimic lead-halide perovskites, we fixed at least one of the B -sites to be a Bi³⁺ cation. The use of O²⁻ anions opens a large combinatorial space of cations to occupy the remaining A and B -sites. We included cations with atomic number less than Bi as possible candidates. We excluded lanthanides and radioactive Tc as possible choices and included all possible oxidation states for multivalent cations. From a simple charge balance, there are 29,515 unique $A'A''B'BiO_6$ double perovskite oxides.

The next step was to screen potential candidates for DFT calculations. We devised a screening criterion based on the structural parameters of the 28 unique $A'A''B'\text{BiO}_6$ double perovskites that have been previously synthesized and were listed in ICSD.²⁷ It should be noted that instead of 1:1:1:1 ratio of A' , A'' , B' and B'' , many entries in ICSD include compounds with varying composition ratios; however, we only used one combination with the composition ratio closest to 1:1:1:1. We used the modified tolerance factor³⁷ ($t = (r_A + r_X) / \sqrt{2}(r_B + r_X)$) and the octahedral factor ($o = r_B / r_X$), where r_A , r_B and r_X are the weighted average radii of A , B and X -site ions, respectively that have been shown to predict the formability in perovskites.³⁸⁻⁴⁰ We used Slater's empirical atomic radii,⁴¹ instead of Shannon's ionic radii⁴² used in conventional definitions³⁷ of o and t , as the former is independent of the coordination environment and oxidation state of an element, which are unknown for a hypothetical perovskite. We find that our simple two-parameter linear regression model – built on o and t structural parameters alone – can accurately describe the formability of all previously known Bi-based double perovskite oxides (reported in ICSD) with an R-squared value of 0.84, as shown in Figure 1b. We used the farthest lying experimental data point (blue) from the fitted line to define a rectangular area and use it as the region of confidence. We find a total of 144 hypothetical $A'A''B'\text{BiO}_6$ double perovskites lying within this region of confidence as shown using red data points in Figure 1b for subsequent geometry optimization. Many of the screened compounds have the same set of o and t values and are overlying in Figure 1b.

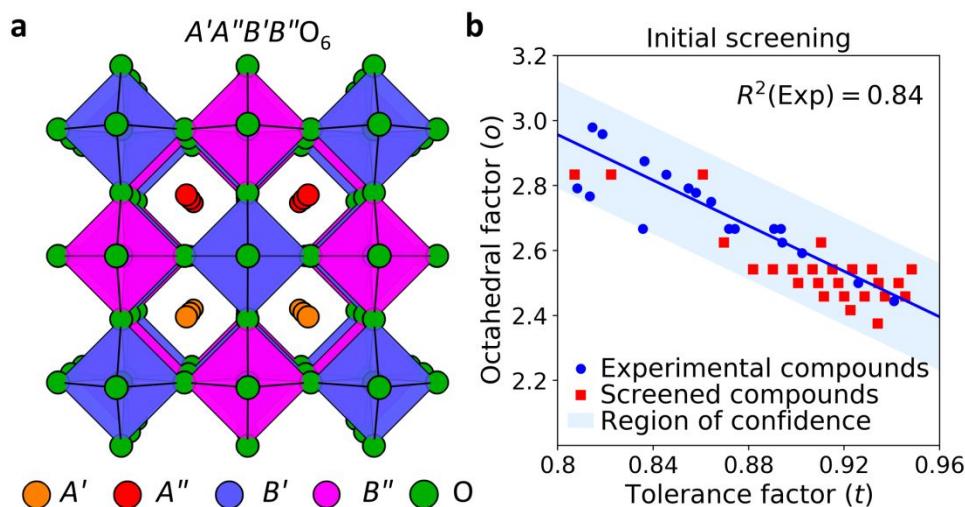


Figure 1. (a) Structure of an ideal double perovskite having layered ordering at the A -site and rock-salt ordering at the B -site. (b) Variation of octahedral factor with tolerance factor for previously synthesized $A'A''B'\text{BiO}_6$ (from ICSD) and for the screened hypothetical compounds conforming to the experimental trend line within the region of confidence.

For the 144 screened $A'A''B'\text{BiO}_6$ double perovskites, we carried out DFT-based geometry optimization in a two-step procedure involving a coarse relaxation followed by a fine relaxation (see the details in the Methods section). For the coarse relaxation, we considered all the hypothetical compounds to be ideal double perovskites without any octahedral tilts. An ideal double perovskite can be classified into one of two space group symmetries: $Fm\bar{3}m$ for $A' = A''$ and $P4/nmm$ for $A' \neq A''$. As shown in Figure 1a, we imposed layered ordering for the A -site cations (A' and A'') and rock-salt ordering for the B -site cations (B' and B''), which are most prevalent in ordered double perovskites.⁴³ We used the same DFT settings as those used in the Open Quantum Materials Database (OQMD)^{32, 44} to enable the calculation of formation enthalpy (ΔH_f) of the hypothetical double perovskites with respect to the most stable reactants, which can be elements or compounds (described in Supporting Information (SI)). In principle, a negative formation enthalpy suggests that a compound is stable and can be synthesized. However, Sun *et*

al.⁴⁵ have recently shown that metastable compounds are fairly common as they report about 90th percentile of the experimental binary oxides lie within 94 meV/atom above the ground state polymorph. Thus, we set a similar criterion to also include metastable $A'A''B'BiO_6$ compounds having $\Delta H_f < 100$ meV/atom that can be expected to be formable. Figure 2a shows the variation of formation enthalpy with tolerance factor for all the screened ideal double perovskites. Within the ideal double perovskite structure, as shown in Figure 2a, only one compound has a negative formation enthalpy: $KBaTeBiO_6$ ($\Delta H_f = -39$ meV/atom) and 21 compounds lie inside the region of formability ($\Delta H_f < 100$ meV/atom).

As mentioned previously, cooperative-tilting of the BX_6 octahedra³⁶ can further stabilize the perovskite structure by lowering the crystal symmetry. The octahedral tilts and their effect on the space group symmetry have been studied extensively for the double perovskite structure⁴⁶⁻⁴⁸ and are summarized in SI (Table S1). For those compounds having $\Delta H_f < 200$ meV/atom, we performed geometry optimization starting from all possible octahedral tilt patterns. We find that for most of the compounds, the ground state has octahedral tilts. As shown in Figure 2b, there are now 36 compounds in the region of formability ($\Delta H_f < 100$ meV/atom) with 5 compounds having a negative formation enthalpy: $KBaTeBiO_6$, $SrBaVBiO_6$, $RbYVBiO_6$, $CsPbMoBiO_6$ and $RbYNbBiO_6$. Of the 36 formable compounds, there are 5 compounds that have the ideal perovskite structure as their ground state.

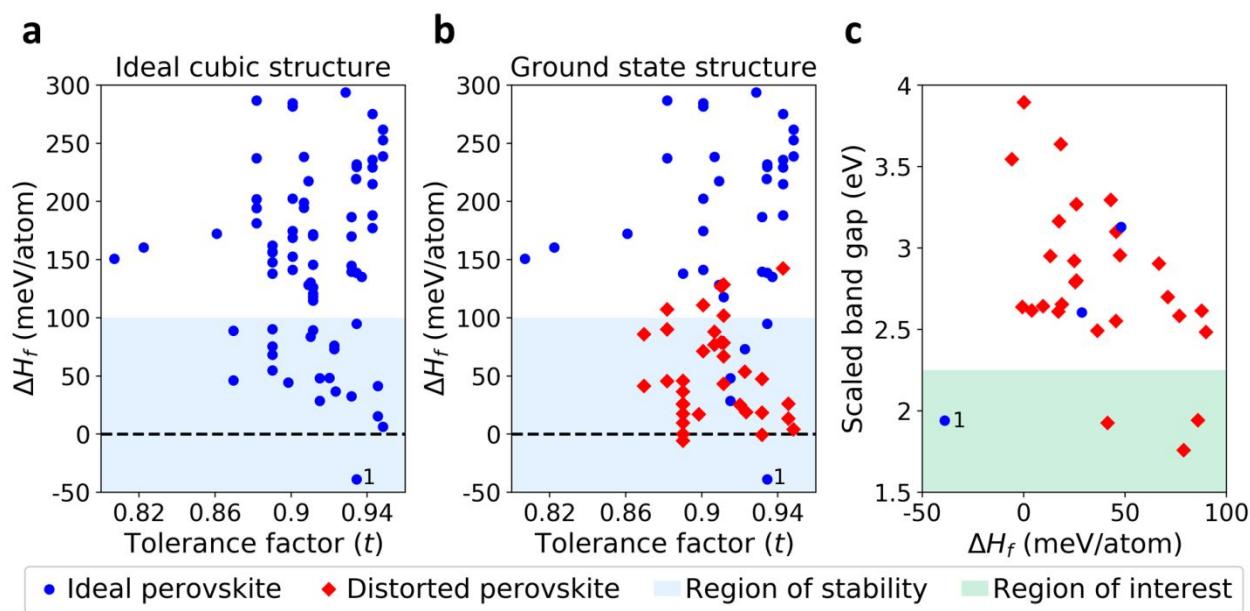


Figure 2. Variation of formation enthalpy (ΔH_f) with tolerance factor for $A'A''B'BiO_6$ compounds with (a) cubic double perovskite structure and (b) the ground state structure with octahedral rotations. (c) Variation of the scaled HSE+SOC band gap with formation enthalpy for the ground state structures of stable $A'A''B'BiO_6$ compounds. The compounds with formation enthalpy lower than 100 meV/atom are considered formable. The marker 1 in (a), (b) and (c) corresponds to $KBaTeBiO_6$.

Any potential candidate for photovoltaic applications, in addition to being formable, should also exhibit an optimal band gap (~ 1.6 eV) and electronic structure for maximum possible absorption of the solar spectrum. GGA functionals, such as the PBE functional,³⁰ are known to underestimate the band gap. To predict experimental band gaps more accurately, we employed the hybrid Heyd-Scucesria-Ernzerhof (HSE06) functional.⁴⁹⁻⁵⁰ We also included spin-orbit coupling effects (SOC), as they are expected to be significant due to the presence of the heavy Bi^{3+} cation. However, as HSE06+SOC calculations are computationally expensive, we used them to calculate the band gap of 25% of the formable compounds. For the remaining formable compounds, we linearly scaled their PBE band gaps ($E_g(PBE)$) using $E_g(HSE+SOC) = 0.87E_g(PBE) + 0.84$, to obtain scaled HSE+SOC band gaps ($E_g(HSE+SOC)$). Such empirical linear scaling has previously

been shown to have a reasonable accuracy for predicting calculated GW band gaps.⁵¹ We show the scaled band gap of the compounds that are below our formability criteria ($\Delta H_f < 100$ meV/atom) in Figure 2c. We find only five compounds in their most stable phase have an intermediate $E_g < 2.25$ eV. Only two of these compounds are lead-free. These two compounds are KBaTeBiO_6 and SrBaVBiO_6 that have calculated E_g of 1.94 and scaled E_g of 2.18 eV, respectively.

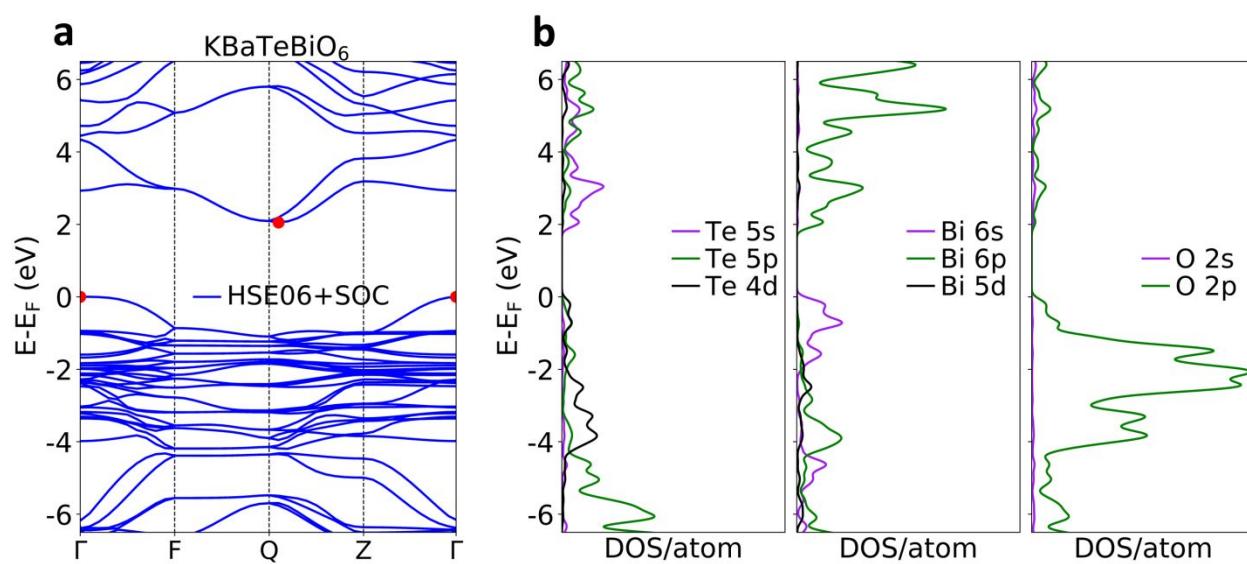


Figure 3. (a) Calculated band structure and (b) atom-projected density of states (DOS/atom) for KBaTeBiO_6 obtained using the HSE06 functional with spin-orbit coupling.

In addition to an optimal band gap, highly dispersed conduction and valence bands are desirable for faster transport of electrons and holes. Based on the calculated band structure, we find SrBaVBiO_6 has flat bands, as shown in SI (see Figure S1). However, KBaTeBiO_6 has widely dispersed bands, as shown in the band structure plot calculated using HSE+SOC (Figure 3a). The atom-projected density of states (DOS) is shown in Figure 3b. KBaTeBiO_6 has a predicted indirect band gap of 1.94 eV from Γ (0, 0, 0) to (0, 0.45, 0.5), which is similar to the calculated indirect

band gap of 2.06 eV (2.62 eV) for $\text{Cs}_2\text{AgBiBr}_6$ ($\text{Cs}_2\text{AgBiCl}_6$).²² The theoretical direct band gap of KBaTeBiO_6 is 2.83 eV and occurs at Γ , whereas the direct band gap of $\text{Cs}_2\text{AgBiBr}_6$ ($\text{Cs}_2\text{AgBiCl}_6$) is 2.45 eV (3 eV). The effective mass of holes in KBaTeBiO_6 is $0.25m_e$ (m_e is the rest mass of an electron) along Γ -Z, which is heavier than that for $\text{Cs}_2\text{AgBiBr}_6$ ($0.14m_e$) and $\text{Cs}_2\text{AgBiCl}_6$ ($0.15m_e$). Whereas the effective mass of electrons for KBaTeBiO_6 is $0.28m_e$ along conduction band minimum (0, 0.45, 0.5) to Q (0, 0.5, 0.5), which is lighter than that of $\text{Cs}_2\text{AgBiBr}_6$ ($0.37m_e$) and $\text{Cs}_2\text{AgBiCl}_6$ ($0.53m_e$). Overall, the low effective masses of electrons and holes for KBaTeBiO_6 points towards favorable carrier transport.

As shown in the DOS plot of KBaTeBiO_6 in Figure 3b, the valence band is predominantly made up of O-2p and Bi-6s states with a small contribution of Te-4d states. The conduction band is largely made up of Bi-6p and Te-5s states with a small contribution from O-2p states. As the Bi 6s anti-bonding states are present at the valence band edge, rather than the conduction band edge, it implies that Bi is in +3 oxidation state, and it can be expected to impart the defect tolerance due to the lone-pair chemistry as discussed earlier.⁵² Furthermore, we find $2.73e$ in the empty conduction-band states of Bi, which supports a +3 oxidation state for Bi. we have described the chemical bonding of KBaTeBiO_6 in detail in SI (see Figure S3). Moreover, a comparison of the calculated absorption spectra of KBaTeBiO_6 and $\text{Cs}_2\text{AgBiBr}_6$ (as shown in Figure S2) shows promising absorbance for the former.

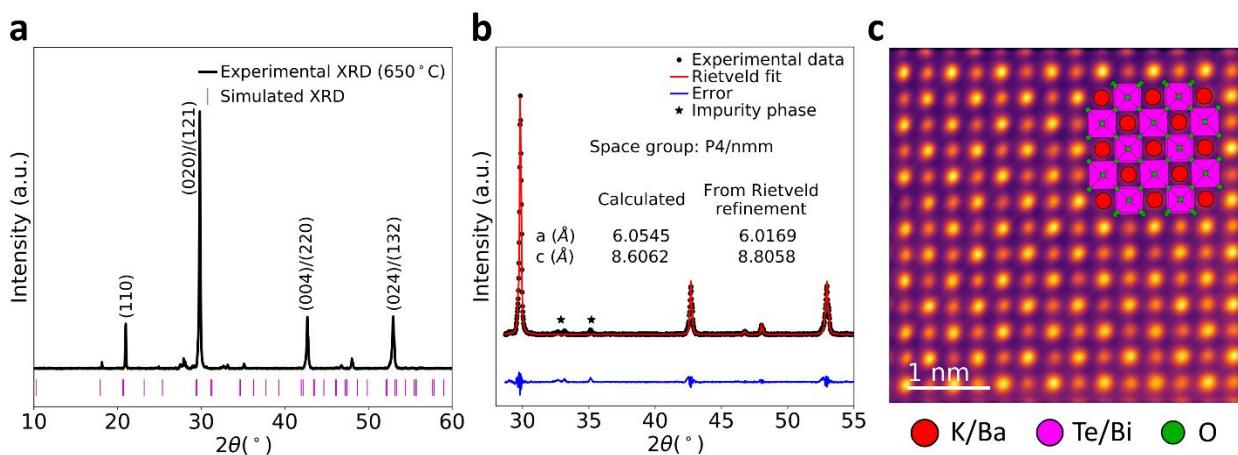


Figure 4. Experimental XRD pattern for KBaTeBiO_6 annealed at 650 °C and the simulated XRD pattern of the DFT-optimized structure. (b) Rietveld refinement of the experimental XRD data and the quality of the fit. (c) Atomic resolution STEM-HAADF image of the KBaTeBiO_6 powder sample with an overlaid atomic model.

Table 1. Atomic positions for KBaTeBiO_6 obtained after Rietveld refinement

Element	Wycoff site	x	y	z
K	2a	0.75	0.25	0.0
Ba	2b	0.75	0.25	0.5
Te	2c	0.25	0.25	0.25529
Bi	2c	0.25	0.25	0.76577
O	8j	0.47965	0.47965	0.2638
O	2c	0.25	0.25	0.02919
O	2c	0.25	0.25	0.48639

To validate our theoretical predictions, we have synthesized KBaTeBiO_6 using a wet-chemistry method (see Methods). We find that annealing at 650 °C is necessary to obtain high phase-purity. Figure 4a shows the X-ray diffraction (XRD) pattern of the samples synthesized at 650 °C and the simulated XRD pattern of DFT-optimized KBaTeBiO_6 unit cell. We chose the

annealing temperature based on the thermogravimetric analysis on the mixed precursors (as shown in Figure S4). The sample annealed at 650°C shows major diffraction peaks at 21.02°, 29.86°, 42.87°, and 53.02° that correspond to (110), convoluted (020)/(112), (004)/(220), and (024)/(132) planes, respectively. Rietveld refinements of the experimental XRD data are provided in Figure 4b. As calculated from DFT, the ground state of KBaTeBiO_6 belongs to $P4/nmm$ space group. The calculated lattice parameters from DFT ($a = b = 6.0545 \text{ \AA}$, $c = 8.6062 \text{ \AA}$) are within 2.3% of the experimental lattice parameters ($a = b = 6.0169 \text{ \AA}$, $c = 8.8058 \text{ \AA}$), as obtained from Rietveld refinement. The refined atomic positions are provided in Table 1.

To investigate the stability of the material, we stored the samples under ambient conditions and performed XRD after 380 days (SI Figure S5). We did not observe any apparent changes in the XRD of the sample, which points towards the excellent stability of KBaTeBiO_6 . To map the chemical composition of the synthesized powder, we have performed EDS using STEM, which confirms the presence of all the five elements. The elemental chemical maps along with their integrated spectrum are shown in Figure S6. To estimate the variability in cation stoichiometry, we have acquired multiple EDS datasets, the findings of which are summarized in Table S2. Instead of an expected 1:1:1:1 cation ratio of K:Ba:Te:Bi, we obtain an average ratio of 0.45 (± 0.028) : 1.32 (± 0.123) : 1.05 (± 0.049) : 1.18 (± 0.157). The composition is normalized such that the total composition of all cations is 4 per formula unit, as in KBaTeBiO_6 . The lower ratio of K could either be due to the presence of K vacancies or excess Te and Bi cations occupying the *A*-site. Further optimization of the synthesis process to control the stoichiometry along with the role of non-stoichiometry on the optoelectronic properties will be the subject of future studies.

To further confirm the formation of the perovskite structure, we have performed atomic-resolution imaging of the synthesized KBaTeBiO_6 particles using aberration-corrected STEM.

Figure 4c shows an atomic resolution high-angle annular dark-field (HAADF) image of the KBaTeBiO_6 lattice along the (001) projection with part of the image overlaid with an atomic model of KBaTeBiO_6 . In HAADF imaging mode, the intensity of every pixel is approximately proportional to the squared atomic number ($\sim Z^2$) of the atomic column.⁵³ As a result, the *B*-site atomic columns containing Te ($Z = 52$) and Bi ($Z = 83$) appear the brightest while *A*-site atomic columns containing K ($Z = 19$) and Ba ($Z = 56$) appear dimmer. The average in-plane lattice parameters obtained from the HAADF image ($a = b = 6.0045 \text{ \AA}$) compare well with those obtained from DFT and XRD. A detailed analysis of intensity profiles in the atomic resolution HAADF image along with atomic-scale chemical composition mapping using electron energy loss spectroscopy (EELS) are provided in the SI (Figures S7 and S8).

After confirming the formation of a perovskite structure, we focus on the optical properties of KBaTeBiO_6 . To determine the experimental optical gap of KBaTeBiO_6 , we measured the absorption spectrum of KBaTeBiO_6 (thin film on a glass slide) using a UV-vis spectrophotometer. The absorption spectrum, as shown in Figure 5a, shows a major onset near 520 nm. The major onset in the measured absorption spectrum is not very sharp, which can be attributed to the indirect band gap as predicted by DFT. We used the Tauc method (shown in the inset of Figure 5a): $(\alpha h\nu)^{1/2}$ vs. $h\nu$; α being the absorption coefficient; to estimate the indirect band gap of KBaTeBiO_6 to be 1.88 eV. As mentioned earlier, the synthesized KBaTeBiO_6 powder exhibits cation non-stoichiometry (deviation from 1:1:1:1 cation ratio), which could have important implications on the material stability and electronic structure. For instance, preliminary DFT calculations at the PBE level show a band gap reduction of 1.18 eV for $\text{K}_{0.625}\text{Ba}_{1.375}\text{Te}_{0.875}\text{Bi}_{1.125}\text{O}_6$ as compared to KBaTeBiO_6 , without introducing any defect states (see Figure S9). $\text{K}_{0.625}\text{Ba}_{1.375}\text{Te}_{0.875}\text{Bi}_{1.125}\text{O}_6$ has a $P\bar{1}$ ground state structure corresponding to a tilt pattern of $a^-b^-c^-$ with a calculated ΔH_f of -148

meV/atom. The lower ΔH_f of $\text{K}_{0.625}\text{Ba}_{1.375}\text{Te}_{0.875}\text{Bi}_{1.125}\text{O}_6$ than KBaTeBiO_6 suggests that the cation non-stoichiometry is thermodynamically favorable. Further investigation on the role of non-stoichiometry, defects and disorder will be the subject of a future study; however, these preliminary DFT results suggest non-stoichiometry to be an effective route to control the electronic structure.

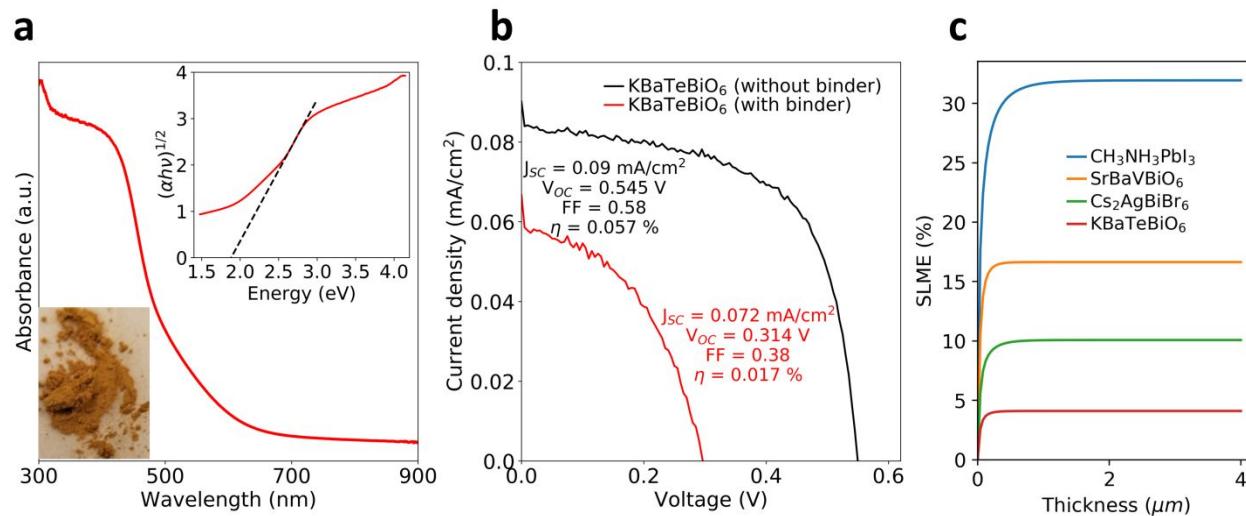


Figure 5. (a) Absorption spectrum of KBaTeBiO_6 film measured using a UV-vis spectrophotometer. The inset shows a Tauc plot with an estimated indirect band gap of 1.88 eV. The bottom left corner of (a) shows the image of the as-synthesized KBaTeBiO_6 powder. (b) J-V characteristics of the most efficient KBaTeBiO_6 photoelectrochemical solar cell fabricated without (red) and with a binder (black). (c) Comparison of variation of calculated spectroscopic limited maximum efficiencies for KBaTeBiO_6 , SrBaVBiO_6 , prototype lead-halide perovskite and bismuth-halide double perovskite.

To demonstrate the applicability of KBaTeBiO_6 as an active absorber layer in solar cells, we have fabricated regenerative PEC solar cells. The device architecture (see Figure S10) is FTO/TiO₂/KBaTeBiO₆/iodide-triiodide/Pt. Two types of devices were fabricated based on the solution preparation of KBaTeBiO_6 , one without any binders in the KBaTeBiO_6 solution and

another with binders for better adhesion of the perovskite particles together as well as with TiO_2 nanoparticles. More details on the solution preparation method can be found in the experimental section. Fig 5b shows the current density (J) -vs. voltage (V) characteristics of the best devices for both cases. The photovoltaic parameters for all the fabricated devices are reported in the SI (Table S3). The devices without binders show superior performance than those with binders possibly due to efficient electron transport from the absorber layer to TiO_2 . The average efficiency obtained for these first-generation devices without binders is $0.038 \pm 0.012\%$ and for the devices with binders is $0.011 \pm 0.007\%$. The highest achieved efficiency of the best device without binders is 0.057%. Compared to other bismuth-based perovskite solar cells that have been reported so far, such as $\text{Cs}_2\text{AgBiBr}_6$ ⁵⁴ ($\eta = 1.04\%$ $E_g = 2.04$ eV), $\text{Cs}_3\text{Bi}_2\text{I}_9$ ⁵⁵ ($\eta = 1.09\%$, $E_g = 2.20$ eV), and $\text{CH}_3\text{NH}_3\text{Bi}_2\text{I}_9$ ⁵⁵ ($\eta = 0.12\%$, $E_g = 2.10$ eV), the efficiency for the best KBaTeBiO_6 device is low. However, KBaTeBiO_6 shows far better material stability than bismuth-based halide perovskites. Furthermore, solar cells using KBaTeBiO_6 nanoparticles show similar performance to those based on high-quality thin films of other inorganic oxide perovskites (summarized in SI Table S4).

To predict the theoretical efficiency of KBaTeBiO_6 that could be achieved by improvements in device fabrication and material optimization, we have calculated its spectroscopic limited maximum efficiency (SLME),⁵⁶ and compared it to cubic-phase $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{Cs}_2\text{AgBiBr}_6$ and SrBaVBiO_6 . We have used the standard AM1.5G solar spectrum at 25 °C for the SLME calculations.⁵⁷ Figure 5c shows the comparison of SLME for the four compounds. The exchange-correlation functionals used for calculating the absorption spectra for $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{Cs}_2\text{AgBiBr}_6$ are PBEsol and HSE+SOC, respectively. These functionals have been chosen as they show the closest agreement to the experimental band gap for respective material systems. For KBaTeBiO_6 , we have calculated the absorption spectra using HSE+SOC.

For SrBaVBiO_6 , we have calculated the absorbtion spectra using PBEsol+SOC and scaled the band gap from 1.52 eV to 2.18 eV (scaled HSE+SOC band gap) using a scissors operator. SLME is a comprehensive predictive metric, which accounts for the difference between the indirect and direct band gaps, the strength of absorption and non-radiative recombination losses to predict the theoretical efficiency of a material. The prototype lead-halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ has an extremely high predicted SLME of 31.69% for a 1 μm thick film, which is due to the sharp absorption onset resulting from a direct band gap. For $\text{Cs}_2\text{AgBiBr}_6$, its indirect band gap and a difference of about ~ 0.5 eV between the indirect band gap and the next allowed direct transition results in an SLME of 10.06% for a 1 μm thick film. In comparison, the calculated SLME of 1 μm thick films of KBaTeBiO_6 is 4.11%. It should be noted that SLME is strongly dependent on the band gap of the material. As mentioned earlier (Figure S9), our preliminary theoretical results suggest that band gap of KBaTeBiO_6 may be tuned by changing the cation stoichiometry, which may lead to even higher SLME. For SrBaVBiO_6 , which has indirect and direct band gaps of 2.18 eV and 2.25 eV, respectively, we find a larger SLME of 16.64% for a 1 μm thick film. While this suggests higher absorbance of the incoming photons in SrBaVBiO_6 , its high effective mass of holes ($0.7m_e$) and electrons ($2.11m_e$), is expected to result in less efficient carrier separation, and potentially lower cell efficiency.

Finally, we briefly discuss various strategies that can lead to improvements in the efficiency of the KBaTeBiO_6 -based solar cells. As we have discussed before, the stoichiometry of the cations has a large impact on the band gap without resulting in defect levels. Hence, control and optimization of the stoichiometry will be an important parameter to achieve higher efficiency. Likewise, control over the oxygen stoichiometry will be another important parameter as oxygen vacancies can either act as shallow donors or lead to deep level defects as observed in wide-band-

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3 gap semiconductors, such as in ZnO .⁵⁸ Another approach could be the growth of high-quality thin
4 films — such as using aerosol-based techniques⁵⁹ — to avoid grain boundaries, which under
5 certain conditions can act as recombination centers in perovskites.¹⁴ Finally, for the PEC-based
6 solar cells, using a compact layer of TiO_2 , as used in solid-state dye-sensitized solar cells, would
7 prevent charge recombination of the excited carriers in the FTO electrode with the oxidized species
8 in the electrolyte.⁶⁰
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17 **Conclusions:**

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20 In summary, using a linear regression analysis and high-throughput DFT calculations, we
21 have predicted a stable Bi-based double perovskite oxide, $KBaTeBiO_6$ from a vast composition
22 space of thousands of compounds which is similar to the prototype halide double perovskites
23 $Cs_2AgBiBr_6$ and $Cs_2AgBiCl_6$. We have successfully synthesized $KBaTeBiO_6$, which crystallizes
24 into a double perovskite structure with excellent stability under ambient conditions. The
25 experimentally measured indirect band gap of $KBaTeBiO_6$ is 1.88 eV, which is similar to the band
26 gap of prototype halide double perovskites $Cs_2AgBiBr_6$ and $Cs_2AgBiCl_6$. In addition to a favorable
27 band gap, $KBaTeBiO_6$ has comparable effective masses of charge carriers to prototype lead-halide
28 perovskites and bismuth-halide double perovskites. The best performing $KBaTeBiO_6$
29 nanoparticles-based regenerative PEC solar cell shows an efficiency of 0.057%. Moreover,
30 preliminary DFT calculations reveal significant electronic structure tunability by varying the
31 cation stoichiometry within the $KBaTeBiO_6$ material system.
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35 In future, the study and control of defects including cation non-stoichiometry and disorder
36 in $KBaTeBiO_6$ will be a crucial task to achieve optimal performance from these semiconductors.
37 More advanced synthesis techniques, such as aerosol routes guided by defect calculation and
38 atomic-scale STEM characterization, will allow us to accomplish this goal. Our study opens up a
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3 large and hitherto unexplored composition space for identifying promising defect-tolerant
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5 semiconductors materials for a variety of optoelectronic applications.
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3 **Supporting Information:**
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20 Calculation of formation enthalpy; octahedral tilts in double perovskites; electronic structure of
21 SrBaVBiO₆; chemical bonding analysis for KBaTeBiO₆; calculated absorption spectra for
22 KBaTeBiO₆; thermogravimetric analysis; stability of as-synthesized KBaTeBiO₆ powder; STEM-
23 EDS analysis; STEM-EELS analysis; effect of non-stoichiometry on electronic structure; device
24 architecture and performance; perovskite oxide-based photovoltaic devices; CIF files of DFT-
25 optimized and Rietveld-refined structures.
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Author contributions:

R.M. conceived and coordinated the project. A.S.T., S.B.C., G.P., and R.M. performed the DFT calculations and analysis. S.K., L-Y.L., M.K. and R.W. carried out the synthesis, experimental characterization and device fabrication under the supervision of P.B. A.S.T., K.A.U, A.Y.B., and R.M. carried out the STEM experiments. A.S.T. and R.M. wrote the paper with contributions from other coauthors. All authors discussed and commented on the manuscript.

Conflicts of interest:

There are no conflicts to declare.

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