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Krishnamoorthy, Thirumal; Ding, Hong; Yan, Chen; Leong, Wei Lin; Baikie, Tom; Zhang, Ziyi; Sherburne, Matthew; Li, Shuzhou; Asta, Mark; Mathews, Nripan; Mhaisalkar, Subodh Gautam

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Lead-free Germanium Iodide Perovskite Materials for Photovoltaic Application

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Thirumal Krishnamoorthy,^{a†} Hong Ding,^{b†} Chen Yan,^{ac†} Wei Lin Leong,^e Tom Baikie,^a Ziyi Zhang,^b Matthew Sherburne,^b Shuzhou Li,^c Mark Asta,^{b*} Nripan Mathews,^{ace*} Subodh G. Mhaisalkar.^{ac}

Computational screening based on density-functional-theory calculations reveals Ge as an element suitable for replacing Pb in halide perovskite compounds with bandgap values suitable for light harvesting. Experimentally, three AGel₃ (A=Cs, CH₃NH₃ or HC(NH₂)₂) halide perovskite materials have been synthesized. These compounds are stable till 150°C, and have bandgaps correlated to the A-site cation size. CsGel₃-based solar cells display higher photocurrents, of about 6 mAcm⁻², but are limited by poor film forming abilities and oxidising tendencies. The present results demonstrate the strong potential of combining computational screening and experimental efforts to develop lead-free halide perovskite compounds for photovoltaic applications.

Following up on initial synthesis of CsPbX₃ (X = Cl, Br or I) perovskites, Weber *et al.* successfully replaced Cs⁺ with methylammonium (CH₃NH₃⁺) cations, opening up a new horizon for the development of inorganic-organic metal-halide perovskite materials.¹ In the past decade, major breakthroughs have come with this series of materials in photovoltaic applications, leading to a rapid increase in the interest in these materials.²⁻⁴ Since 2009, the power conversion efficiency of devices based on inorganic-organic perovskites has leapt from 3.8% to the most recent highest certificated value of 20.1%.⁵⁻⁷ This value has surpassed the efficiencies of devices based on amorphous silicon and is almost on par with those using CdTe or CIGS. With such promising device efficiency, low cost of starting materials and simple solution processing, organic-inorganic halide perovskites are a strong alternative to conventional photovoltaics. One key concern for future large-scale manufacturing and commercialization of current

perovskite-based photovoltaic devices is that they may release Pb into the environment. For example, in a scenario of solar cell encapsulation rupture, Pb ions may dissolve into rainwater causing significant environmental impact. In this context, future commercial utilization requires replacement of Pb in the perovskite structure, while maintaining analogous optical and photovoltaic performance.⁸⁻⁹

In the present work, high-throughput computational methods based on density-functional theory (DFT) were used to screen for candidate inorganic halide perovskites AMX₃, with desirable bandgaps and chemical stability. A total of 360 AMX₃ chemical composition were considered, with A¹⁺ and X¹⁻ ions chosen from {K, Rb and Cs} alkali metals and {Cl, Br and I} halogen elements, respectively, in combination with 40 candidate divalent M-site cations. First-principles calculations were performed within the framework of DFT employing the projector augmented wave method and the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation for the exchange-correlation energy, as implemented in the Vienna ab initio simulation package^{10, 11-13}. The computed PBE bandgaps (E_g^{PBE}) are illustrated in Fig. 1. Although the bandgaps predicted from PBE-DFT calculations are expected to underestimate the true values measured experimentally, the computational screening exercise uses the values of E_g^{PBE} to explore overall trends across the different chemistries. Further, we note that our team has successfully fabricated CsSnI₃ perovskite solar cells and achieved high photocurrent densities under simulated full sunlight. The experimentally measured bandgap of CsSnI₃ was 1.3 eV¹⁴⁻¹⁵, while the calculated value is $E_g^{PBE} = 0.44$ eV for cubic CsSnI₃. We thus use this compound as a calibration point for our calculations, and search for other AMX₃ chemical compositions with E_g^{PBE} in the range of 0.2 - 0.7 eV. From the results of the computational screening exercise, considering only the calculated bandgap values, we identified 9 candidate

^a Energy Research Institute @ NTU (ERI@N), Research Techno Plaza, X-Frontier Block, Level 5, 50 Nanyang Drive, 637553, Singapore

^b Department of Materials Science and Engineering, University of California, Berkeley, USA

^c School of Materials Science and Engineering, Nanyang Technological University, Nanyang Avenue, 639798, Singapore

^e Institute of Materials Research and Engineering (IMRE), Agency for Science, Technology and Research (A*STAR), 3 Research Link, Singapore 117602, Singapore

[†] These authors contributed equally to this work.

*Address correspondence to: mdasta@berkeley.edu, Nripan@ntu.edu.sg

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compositions: KSnBr_3 , KSnI_3 , RbSnBr_3 , RbSnI_3 , CsSnBr_3 , KGeBr_3 , KGeI_3 , RbGeI_3 and CsGeI_3 . The thermodynamic stability of these compositions were further evaluated through the Materials Project database¹⁶ with calculated energies to determine whether the AMX_3 compositions would decompose to simpler binary phases. We found that only three of the candidate compositions, namely RbSnBr_3 , CsSnBr_3 and CsGeI_3 , are predicted to be energetically stable (as shown in Table S1).

Due to the significant underestimation of bandgaps by the PBE method, we repeated the computational screening exercise described in the previous paragraph employing the Δ -sol approach [24], which features comparable computational cost to PBE, but with improved accuracy for bandgap prediction. Specifically, we calculated by the Δ -sol method the bandgaps of all compounds for which $E_g^{\text{PBE}} > 0.1$ eV, identifying all with calculated values within 20% of that for CsSnI_3 . Of these, the compounds that were predicted to be energetically stable were the same as those identified from PBE, namely RbSnBr_3 , CsSnBr_3 and CsGeI_3 .

Sn-based perovskites have been considered in the literature to a much greater degree than Ge-based halide perovskites. Hence, in subsequent experimental work we focussed attention of the potential applications of Ge-based halide perovskite compound for solar cells.

Figure 1: Predicted PBE functional band gaps of the 360 AMX_3 halide perovskite compositions. The top, middle and bottom section correspond to X-site species with halogens $X = \text{Cl}$, Br and I , respectively, and in each session, the x and y axes correspond to M and A-site components.

Figure 2: Pawley fit of the powder X-ray diffraction patterns of (a) CsGeI_3 , (b) MAGeI_3 and (c) FAGeI_3 confirming single-phase samples adopting rhombohedral symmetry ($R3m$) at room temperature. (d) Crystal structure adopted by the AGeI_3 perovskite.

Experimentally, we have synthesized both the inorganic germanium halide perovskite (CsGeI_3), as well as alternative hybrid perovskites where the A^+ cation is replaced with methylammonium (MA) and formamidinium (FA) molecules (See SI for detailed procedure). Fig (2a, b, c) shows the X-ray diffraction characterization of the three different synthesized samples which can all be indexed to trigonal cells (with $R3m$ space group symmetry), in good agreement with previous reports.¹⁷⁻¹⁸ Extracted lattice parameters of rhombohedral unit cells can be seen in Fig. S3. We note that the room temperature CsGeI_3 rhombohedral crystal structure ($a = 5.98$ Å and $\alpha = 88.6^\circ$), is very close to the cubic perovskite structure considered in the calculations ($a = 5.99$ Å and $\alpha = 90^\circ$). The replacement of Cs with larger MA or FA molecules leads to a rhombohedral angle (α) that is further away from 90° . The increased structural distortions due to cation replacement are also consistent with the prediction based on empirical perovskite tolerance factors which shows a larger deviation from one with larger A-site cation. Many of the halide perovskites exhibit multiple phase transitions at temperature ranges achievable by a solar cell under external operating conditions. This structural phase transition is expected to influence the electronic band structure of the material and therefore impact the photovoltaic properties. The long-term stability of the device may also have an effect because of the change in volume of the crystal.¹⁹ Contrastingly, variable temperature XRD measurements in the Germanium halides reveal no structural change to a higher symmetry cubic system for any of the Ge samples investigated (as shown in Figs. S3). For each perovskite, an increase in temperature resulted in a corresponding increase in angle α towards 90° , however complete sample decomposition was observed before a 90° angle, and hence a cubic system could not be obtained. Although the perovskite tolerance factor can be a useful guide to predict the stability of the perovskite structure-type, it does not take into account distortions arising from electronic contributions, e.g. the influence of stereochemically active $n\text{S}^2$ lone-pair electrons that generally become more pronounced through the Pb^{2+} , Sn^{2+} and Ge^{2+} series. In this context, detailed structural investigations are still required to elucidate the symmetry properties of these materials, and will form part of our future work.²⁰⁻²¹

Fig. S4 shows the TGA curve of all three Ge-based perovskite compounds collected under nitrogen atmosphere. CsGeI_3 shows higher stability (up to around 350°C) in comparison with the other two hybrid perovskites (up to around 250°C). MAGeI_3 follows a single step degradation pathway. This single step could account for the sublimation of the perovskite, but when the material was heated in a glass petri dish at around 250°C (in an inert atmosphere) white fumes were released first, immediately followed by orange fumes. So it is clear that MAGeI_3 decomposes first and the decomposed product goes in to vapour state. Comparatively, FAGeI_3 exhibited less stability and follows a two stage degradation pathway where the first weight loss of 44 % was consistent with the complete transformation to GeI_2 . Differential scanning calorimetric

analysis demonstrates the stability of all three perovskite compounds in the range of device working temperatures.

Fig. 3(a) shows the Tauc plot of germanium perovskites. With increasing size of the A^+ cation in the structure, the colors of the compounds change from black to red and then orange for Cs^+ , MA^+ and FA^+ based perovskites. Estimated values of the band gap derived from Tauc plots are 1.63, 2.0 and 2.35 eV for $CsGeI_3$, $MAGeI_3$ and $FAGeI_3$, respectively. Although the three compounds have bandgaps greater than the ideal one predicted by the Shockley-Queisser limit, $CsGeI_3$ which has a bandgap slightly higher than $CH_3NH_3PbI_3$ could be of great interest. The other larger bandgap perovskites could be good candidates for achieving high open circuit voltage required for making tandem solar cells. The experimentally measured bandgap of $CsGeI_3$ is about 0.4 eV higher than $CsSnI_3$, which agrees well with the trends in the calculated PBE bandgaps, as shown in Fig. 1. The computed band structure of cubic $CsGeI_3$, as well as projected density of states, is plotted in Fig. 3(b). It can be seen that a direct band gap is located at the R-(0.5, 0.5, 0.5) point of the Brillouin zone. The valence band maximum is primarily Ge-s in character, with some hybridization with I-s states, while the character of the states at the conduction band minimum is dominated by Ge-p states. This suggests that the light-absorption would result in an electronic transition that would occur majorly between Ge bonding and antibonding orbitals. This kind of "intra-atomic" band gap behaviour, where increase of the lattice constant will give rise to further energy splitting between these orbitals and corresponding increase in the bandgap of the materials (as noted within these Germanium halide perovskites). The band gap deformation potential $a_g = dE/d\ln a$ is calculated as 10.05 eV, which is larger than the values reported for Sn-based perovskites²². This suggests the potential for larger bandgap tuning by cation substitution in Ge-based perovskites.

Figure 3. (a) Optical absorption spectrum of $CsGeI_3$, $MAGeI_3$ and $FAGeI_3$, in comparison with $CsSnI_3$. (b) Calculated band structure and projected density of states of $CsGeI_3$. The energy of the highest occupied state is set to 0 eV. (c) Photoelectron spectroscopy in air (PESA) of powder samples and (d) Schematic energy level diagram of $CsGeI_3$, $MAGeI_3$ and $FAGeI_3$.

Photoemission spectroscopy in air was used to measure the valence band energy level of all these three Ge-based perovskite compounds and shown in Fig. 3c. The measured values of valence band (VB) of $CsGeI_3$, $MAGeI_3$ and $FAGeI_3$ perovskites are -5.10, -5.2, and -5.5 eV respectively and from the observed optical band gap values, the conduction bands (CB) are calculated to be -3.47, -3.2 and -3.15 eV, respectively as shown in Fig. 3d. The replacement of Cs with MA and FA molecules decreases the valence band level and this follows the same trend as in other metal halide systems.^{8,14,23} It must be noted that slight oxidation of the samples during the PESA measurements may have occurred.

Figure 4 (a) J-V curves of photovoltaic devices fabricated with different germanium halide perovskites. (b) IPCE spectrum of $MAGeI_3$ device.

We further fabricated solar cells with the germanium iodide perovskites using compact and mesoporous TiO_2 and Spiro-OMeTAD as electron- and hole-selective contacts, respectively. Cross-sectional SEM image of device architecture is shown in Fig S5. However, dissolution of germanium perovskites in most organic polar solvents is not satisfactory due to the presence of hygroscopic phosphorous oxoacids as confirmed by FTIR spectrum results (Fig. S6). Phosphorous acid (added as a reducing agent) with its OH group is involved in hydrogen bonding with iodide, making it very challenging to extract it. Films fabricated with the semi-transparent solutions of perovskites in dimethylformamide (DMF) are shown in Fig. S5. $CsGeI_3$ and $MAGeI_3$ have relatively smooth morphology while that of $FAGeI_3$ is very poor. The current density-voltage ($J-V$) characteristics of the photovoltaic devices are shown in Fig. 4(a) and Table 1. Our devices exhibit photocurrent density of 5.7 mAcm^{-2} and 4 mAcm^{-2} for $CsGeI_3$ and $MAGeI_3$ compounds respectively as shown in Fig. 4(a). These values are encouragingly higher than that derived from the pristine Sn-based perovskite compounds. However, the solar cells suffered from very poor open circuit voltages. The poor performance of the devices could be attributed to Ge^{4+} formation by oxidation (supported by XPS measurements as shown in Figs. S7 & S8) during the synthesis and fabrication procedures. The poor solubility of these compounds in polar solvents is an additional limiting factor. Due to the poor film quality of $FAGeI_3$ shown in Fig S5, solar cells did not show any photocurrent. Due to the instability $CsGeI_3$ film in ambient atmosphere, only IPCE measurements of $MAGeI_3$ device were performed (Fig. 4(b)). It can be seen that the device was responsive from about 620 nm and the integrated photocurrent (3.7 mAcm^{-2}) corresponded well with the short circuit current density. Newer preparation methods of Ge-

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based perovskite without the addition of hypophosphorus acid and under strict control of synthesis atmosphere, precursors may lead to significant improvement of the film quality and the corresponding device performance. Another possibility is to form the devices through vacuum evaporation, although the challenges of disproportionation also need to be considered. This should be combined with a judicious choice of the HTM to ensure efficient hole extraction.

Device	J_{sc} (mAcm ⁻²)	V_{oc} (mV)	FF (%)	PCE (%)
CsGeI ₃	5.7	74	27	0.11
MAGeI ₃	4.0	150	30	0.20

Table 1. Photovoltaic performance parameters of perovskite solar cells based on CsGeI₃ and MAGeI₃ materials under simulated full sunlight of 100 mWcm⁻²

In summary, high-throughput computational screening has suggested that germanium may act as suitable replacement for lead in halide perovskite materials for solar cell applications. Experimentally CsGeI₃ crystals with stable rhombohedral crystal structures have been synthesized, which do not show phase changes in the range of device working temperatures. Further, we also synthesized MAGeI₃ and FGeI₃ crystals and compared their crystal structure, band gap, and thermal stability. Solar cell exhibited photocurrent values of 5.7 and 4 mAcm⁻² for CsGeI₃ and MAGeI₃, respectively. Overall, the results of the present study demonstrate a strong potential for Ge-based halide perovskite compounds in photovoltaic applications.

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References

- Weber, D. Z. *Naturforsch* **1978**, *33b*, 1443.
- Jeon, N. J.; Noh, J. H.; Yang, W. S.; Kim, Y. C.; Ryu, S.; Seo, J.; Seok, S. I. *Nature* **2015**, *517*, 476.
- Krishnamoorthy, T.; Kunwu, F.; Boix, P. P.; Li, H.; Koh, T. M.; Leong, W. L.; Powar, S.; Grimsdale, A.; Gratzel, M.; Mathews, N.; Mhaisalkar, S. G. *J. Mater. Chem. A* **2014**, *2*, 6305.
- Xing, G.; Mathews, N.; Sun, S.; Lim, S. S.; Lam, Y. M.; Grätzel, M.; Mhaisalkar, S.; Sum, T. C. *Science* **2013**, *342*, 344.
- Yang, W. S.; Noh, J. H.; Jeon, N. J.; Kim, Y. C.; Ryu, S.; Seo, J.; Seok, S. I. *Science* **2015**.
- Burschka, J.; Pellet, N.; Moon, S.-J.; Humphry-Baker, R.; Gao, P.; Nazeeruddin, M. K.; Gratzel, M. *Nature* **2013**, *499*, 316.
- Kim, H. S.; Lee, C. R.; Im, J. H.; Lee, K. B.; Moehl, T.; Marchioro, A.; Moon, S. J.; Humphry-Baker, R.; Yum, J. H.; Moser, J. E.; Grätzel, M.; Park, N. G. *Scientific Reports* **2012**, *2*.
- Hao, F.; Stoumpos, C. C.; Cao, D. H.; Chang, R. P. H.; Kanatzidis, M. G. *Nat Photon* **2014**, *8*, 489.
- Noel, N. K.; Stranks, S. D.; Abate, A.; Wehrenfennig, C.; Guarnera, S.; Haghighirad, A.-A.; Sadhanala, A.; Eperon, G. E.; Pathak, S. K.; Johnston, M. B.; Petrozza, A.; Herz, L. M.; Snaith, H. J. *Energy Environ. Sci.* **2014**, *7*, 3061.
- Kresse, G. *J Non-Cryst Solids* **1995**, *193*, 222.
- Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys Rev Lett* **1996**, *77*, 3865.
- Blöchl, P. E. *Physical Review B* **1994**, *50*, 17953.
- Kresse, G.; Joubert, D. *Physical Review B* **1999**, *59*, 1758.
- Kumar, M. H.; Dharani, S.; Leong, W. L.; Boix, P. P.; Prabhakar, R. R.; Baikie, T.; Shi, C.; Ding, H.; Ramesh, R.; Asta, M.; Graetzel, M.; Mhaisalkar, S. G.; Mathews, N. *Advanced Materials* **2014**, *26*, 7122.
- Sabba, D.; Mulmudi, H. K.; Prabhakar, R. R.; Krishnamoorthy, T.; Baikie, T.; Boix, P. P.; Mhaisalkar, S.; Mathews, N. *J. Phys. Chem. C* **2015**, *119*, 1763.
- Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G.; Persson, K. A. *Apl Mater* **2013**, *1*.
- Thiele, G.; Rotter, H. W.; Schmidt, K. D. *Z. Anorg. Allg. Chem.* **1987**, *545*, 148.
- Stoumpos, C. C.; Fraser, L.; Clark, D. J.; Kim, Y. S.; Rhim, S. H.; Freeman, A. J.; Ketterson, J. B.; Jang, J. I.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2015**, DOI:10.1021/jacs.5b01025.
- Binek, A.; Hanusch, F. C.; Docampo, P.; Bein, T. *J. Phys. Chem. Lett.* **2015**, *6*, 1249.
- Kieslich, G.; Sun, S.; Cheetham, A. K. *Chem. Sci.* **2014**, *5*, 4712.
- Stoumpos, C. C.; Fraser, L.; Clark, D. J.; Kim, Y. S.; Rhim, S. H.; Freeman, A. J.; Ketterson, J. B.; Jang, J. I.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2015**.
- Huang, L.-y.; Lambrecht, W. R. *Phys Rev B* **2013**, *88*, 165203.
- Koh, T. M.; Fu, K.; Fang, Y.; Chen, S.; Sum, T. C.; Mathews, N.; Mhaisalkar, S. G.; Boix, P. P.; Baikie, T. *J. Phys. Chem. C* **2014**, *118*, 16458.
- Chan, M. K. Y.; Ceder, G. *Phys. Rev. Lett.* **2010**, *105*, 196403.

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Thirumal Krishnamoorthy,^{a†} Hong Ding,^{b†} Chen Yan,^{ac†} Wei Lin Leong,^d Tom Baikie,^a Ziyi Zhang,^b Matthew Sherburne,^b Shuzhou Li,^b Mark Asta,^{c*} Nripan Mathews,^{abe*} Subodh G. Mhaisalkar.^{ab}

We demonstrate strong potential of computational screening and Germanium iodide perovskite compounds for photovoltaic application