Monte-Carlo Study of Ion-Sputtering Parameters and Ab-Initio Calculations of Selected Perovskites for Solar-Powered Electricity

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Abstract. Attributable to efficiencies as high as 25.2%, organic inorganic hybrid perovskite has become the quickest developing solar technology, rivalling the conventional photovoltaic technology. Although, they are unique and remarkable, stability concern and toxic behaviour of perovskites impede mass production. With this impetus of realizing a non-toxic perovskite, a new approach was proposed by performing Monte Carlo simulations. In this paper, this approach was further studied with an First principles investigations using the plane-wave pseudopotential method within the density functional theory (DFT) as employed in Quantum ESPRESSO (QE) software package. Mechanical and electronic properties of $\text{CH}_3\text{NH}_3\text{PbBr}_3$, $\text{CH}_3\text{NH}_3\text{SnBr}_3$, $\text{CH}_3\text{NH}_3\text{SnI}_3$, and $\text{CH}_3\text{NH}_3\text{PbI}_3$, perovskites were investigated. Lattice constants were calculated to understand the mechanical properties, while band gaps were calculated to shed more light on their electronic properties. Our results were compared with the experimental and theoretical values and found a good agreement between them. These indicated that the two materials were remarkably similar and that Sn was a good substitute for Pb in solar cell perovskite materials.

Keywords: Perovskite; Lead-free; Sputtering; Density Functional Theory; HOIP solar cells; Band structure; computer simulation

1. Introduction

In the past decade, both theorist and experimentalist have devoted attention to metal-halide perovskites because of the enormous prospective over silicon-based photovoltaics and also, for tuneable opto-mechanical applications in tech-device fabrications tremendous imminent over silicon-based photovoltaics and furthermore, for tuneable opto-mechanical applications in tech-gadget manufactures [1-2]. Methyl ammonium lead iodide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$), is a hybrid organic
inorganic perovskite (HOIP) material and has been proclaimed as one of the significant revelations by specialists in 2013 [3]. The power conversion of this cell has gotte to 25.2% in 2020[4].

Presence of lead, couple with stability issues hampers large scale production. Several theoretical and experimental attempts have been made to totally or partially replace lead, however, as at now, none of these attempts has led to the discovery of non-toxic, lead-free and stable perovskites that have similar optoelectronic properties to lead-based perovskites. Previous studies include the total replacement of Pb\(^{2+}\) with Sn\(^{2+}\) [9,10]; the partial replacement of Pb\(^{2+}\) with Ge\(^{2+}\) [17] [18]; Ca\(^{2+}\); Sr\(^{2+}\); Cd\(^{2+}\); and Bi-Tl to mention a few.

To overcome this challenge, we concentrated on ion beam sputtering, a vacuum process. Ion-Beam Surface Sputtering (IBSS) of materials is currently a highly intensive area of research because it is a less expensive way of surface investigation, processing and production of nanostructures for opto-mechanical and electronic use [17-21]. A Recommendation of a novel radio-frequency-sputtering technique of methylammonium halides fabrication was suggested by ref 22 and ref 23. And they reiterated that same characteristics were displayed by sputter processed perovskite films when compared to perovskites made via solution-processess counterparts and a higher PCEs were produced. However, sputtering method of perovskite production can be expensive and time-consuming, and recent soft-ware has made it easier to study sputtering characteristics of materials and thus better understand the sputtering characteristics of materials. Before widespread computer use, experimentation was the only method of understanding the elusive nature of damage in materials. Recent nuclear materials studies frequently utilize simulations. One of the examples is Gunay, 2013 [24], who utilized Monte Carlo (MC) methods to understand the neutronic performance of fuels.

Sputtering is the process by which atoms of target materials are bombarded with incoming ions thereby setting off secondary cascades that culminates to thermal and kinetic agitations of atoms of the target material. The frequently used gas ions for sputtering experiments are noble gas ions because they do not cause surface composition changes which often lead to unusual morphology [18, 25].Molecular dynamic simulations are the major features in sputtering process. It is seen that collisional data are developed and exploited in MC simulation methodologies [25, 26]. A Monte Carlo simulation suite developed by ref 26 and 27, TRansport of Ions in Matter (TRIM) is an example.

Also, to study the mechanical and structural properties of the selected perovskite materials, we used the plane-wave pseudopotential method within the density functional theory (DFT) method[28].Theoretically, GGA-PBE slightly underestimate band gaps [29, 30], whereas there is a submission that GGA-PBEsol and hybrid functional underestimate and also overshoot the band gap [31, 32]. Besides, PBE functional alone [33] gives electronic band structure analogous to hybrid functional’s with great accuracy and less computational stress [34]. So in this work, we used only GGA-PBE exchangecorrelation functional.

We have studied the sputtering yield of Argon ion in CH\(_3\)NH\(_3\)PbI\(_3\), CH\(_3\)NH\(_3\)SnI\(_3\), CH\(_3\)NH\(_3\)GeI\(_3\), CH\(_3\)NH\(_3\)Mgl\(_3\), CH\(_3\)NH\(_3\)CaI\(_3\), CH\(_3\)NH\(_3\)PbBr\(_3\), CH\(_3\)NH\(_3\)SnBr\(_3\) and CH\(_3\)NH\(_3\)GeBr\(_3\) perovskites, for a range of angle of incidence and ion energies, by employing a Monte Carlo simulation, using TRIM. The electronic band structural and mechanical properties of the selected perovskite materials were calculated too. Inert gases ions were used in the sputtering process.

2. Methodology

The research used two simulation techniques. Stoppage and Range of Ions in Matter (SRIM) for sputtering calculations and quantum Espresso for optical and bands structure calculations. The specific simulation details behind each software used (SRIM and Quantum Espresso) and the overall structure
were explained in this section. The entirety of the theoretical context for the calculation algorithms are embedded in the TRIM package and are accessible in the papers by Ziegler and Biersack [27]. Ion energies in sputtering experiments normally range within 10 keV. The set up for the experiment is in three steps:

1. The ion beam parameters: the incoming ion used is Argon (Ar). The ion energy used is 5 keV and the angle of incidence is 78°. Monolayer Collision Steps / Surface Sputtering is the type of TRIM calculation used.

2. Target parameters: the targets were lead perovskite CH₃NH₃PbI₃, CH₃NH₃SnI₃, CH₃NH₃GeI₃, CH₃NH₃MgI₃, CH₃NH₃CaI₃, CH₃NH₃PbBr₃, CH₃NH₃SnBr₃ and CH₃NH₃GeBr₃, density of 3.83/cm³ [13] was used for CH₃NH₃PbBr₃ instead of TRIM calculated density of 1.48, as recommended by ref 14. For the remaining perovskites, density used are 3.32 g/cm³, 2.82 g/cm³, 3.42 g/cm³, 2.87 g/cm³, 2.58 g/cm³, 2.08 g/cm³ and 2.06 g/cm³, respectively. The TRIM was set up with perovskite wafer thickness of 35 nm and perovskites were built from their composites in the stoichiometric ratio 1:3:1:3:1:3 for C, H, N, H, Pb/Sn/Ge/Mg/Ca and I/Br, respectively. An amount of 1000 ions was used for each simulation in order to allow the simulation to run for a reasonably long time [14].

3. The output or special parameters: the Plotting window depth was 35 nm, the stopping power version used was SRIM-2008 and output disk storage files were set.

While the structural and mechanical properties of the selected perovskites were examined by using the plane-wave pseudopotential (PP) method within the density functional theory as employed in Quantum ESPRESSO (QE) software package [28]. Methylammonium lead iodide (MALI), methylammonium tin iodide (MATI), methylammonium lead bromide (MALB) and methylammonium tin bromide (MATB) perovskites in the cubic phase, Pm̅3m, were examined for their structural and electronic properties. MALI undergoes structural phase transitions from orthorhombic Pnma to tetragonal I4/mcm at ~170 K and then to cubic Pm 3m at ~330 K [37]. We used a cubic space group Pm̅3m since at ambient conditions, these perovskites have the cubic space group [38]. For the total energy calculations, the optimized plane-wave cut-off energy of 680 eV and a 4 × 4 × 4 Monkhorst-Pack K-grid mesh are used for the atomic relaxation calculations for all the compounds under consideration in cubic Pm̅3m phase. The whole atomic positions are relaxed until the Hellmann-Feynman forces on each atom become less than 20 meV/Å. The tetrahedron method with Błöch corrections [39], is employed to compute the density of state (DOS) for each perovskites. The calculations were carried out as follows:

1. Convergence tests for automatically generated Monkhorst-Pack K-point scheme [39] and Kinetic cutoff energy were carried out for all the structures to determine the optimum simulation parameters.

2. Structure optimization (or geometry optimization) was carried out for the four different structures to obtain the ground state energy (minimum force) suitable for QE to predict the ground state properties (such as; bandgaps, lattice constants and band structure) of these systems. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization technique [36], was used to obtain the ground-state energies and the optimal crystal structures of these considered compounds.
3. After all the different optimizations were achieved, the bandgaps for the different fully optimized structures were calculated by running a Non-Self-Consistent Field (NSCF) calculation.

3. Results and discussion

In this section, we will be presenting and discussing the results of B-site sputtering and X-site sputtering. Table 1 is showing the sputter yield results when Argon ion was used to bombard these selected perovskites at ion angle of 78°.

Table 1: Perovskite material’s sputter yield at 78° ion incidence angle.

| Perovskite Materials | Yield at 78° (atoms/ion) | Experimental PCE (%) |
|----------------------|---------------------------|-----------------------|
| CH₃NH₃PbI₃          | 1.25                      | 25.2                  |
| CH₃NH₃SnI₃          | 1.14                      | 6.4                   |
| CH₃NH₃GeI₃          | 1.09                      | 0.2                   |
| CH₃NH₃MgI₃          | 1.51                      | -                     |
| CH₃NH₃CaI₃          | 1.5                       | -                     |
| CH₃NH₃PbBr₃         | 1.31                      | -                     |
| CH₃NH₃SnBr₃         | 1.16                      | -                     |
| CH₃NH₃GeBr₃         | 1.15                      | -                     |
| CH₃NH₃MgBr₃         | 1.71                      | -                     |
| CH₃NH₃CaBr₃         | 1.74                      | -                     |

The sputter yield of lead (Pb) in methylammonium lead iodide, at 78° incidence angle was calculated to be 1.25 atoms/ion, tin (Sn) in methylammonium tin iodide was 1.14 atoms/ion, 1.09 atoms/ion is the sputter yield of germanium when methylammonium germanium iodide was sputtered with 5 keV Argon ion at 78° ion incidence. While 1.51 atoms/ion and 1.5 atoms/ion, are for magnesium and calcium in methylammonium magnesium iodide and methylammonium calcium iodide, respectively.

Sputtering yield values of 1.31 atoms/ion, 1.16 atoms/ion, 1.15 atoms/ion, 1.71 atoms/ion and 1.74 atoms/ion were recorded for lead (Pb), tin (Sn), germanium (Ge), magnesium (Mg) and calcium (Ca), for lead, tin, germanium, magnesium and calcium bromide perovskites, respectively.
In Fig. 1, the yield was decreasing as the recorded experimental PCEs were decreasing. However the yield values started increasing for the remaining metals, Mg and Ca.

The same inference was seen when the X-site was changed from Iodine (I) to Bromine (Br), in fig 2. The yield was decreasing but started increasing for the remaining metals, Mg and Ca, probably due to the fact that they are in different group on the periodic table.

The structural and electronic properties of lead-based and Tin-based hybrid halide perovskites were done to further investigate the appropriateness of tin in tin-based perovskites, in the replacement
of lead in lead-based perovskite materials by using Ab initio approach. We started MALI and MATI which served as reference material, then MALB and MATB perovskites in the cubic phase \(Pm\bar{3}m\). So, we performed quantum mechanical simulations on two lead based perovskite and two tin based perovskites.  

The convergence test for total minimum energy as a function of cut-off energy is performed with an increment of 10 Ry in the range of 20 to 100 Ry. While varying the energy cut off, the other parameters in the input file are fixed.  

**Structural Optimization**  
For good total minimum energy convergence, we have used the criteria that the change in energy (\(\Delta E\)) from the minimum energy at the reference point (100 Ry) to be approximately equal to \(4 \times 10^{-4}\) Ry per atom. In our calculation, \(\Delta E = 4.43 \times 10^{-4}\) per cell \((8.86 \times 10^{-5}\) Ry per atom) for \(CH_3NH_3PbI_3\) at 40 Ry energy cut-offs and convergence is achieved. Moreover, \(\Delta E = 4.13 \times 10^{-4}\) per cell \((8.26 \times 10^{-5}\) Ry per atom) for MATB at 40 Ry energy cut-offs and the energy is converged.  

For the total energy calculations, the optimized plane-wave cutoff energy of 680 eV and a \(4 \times 4 \times 4\) Monkhorst-Pack K-grid mesh are used for the atomic relaxation calculations for the compounds under consideration in cubic \(Pm\bar{3}m\) phase. Variation of the value of lattice constant around the experimental value fixing other parameters was done. The optimized equilibrium lattice constant of MALI and MATI in cubic phase is 6.26 (Å) and 6.31 (Å), respectively which are in good agreement with other experimental results [42, 43]. Similarly, the calculated equilibrium lattice constant of MALB and MATB are 6.12 (Å) and 6.04 (Å), which are all a bit larger than the experimental value mentioned [43]. From the DFT calculations, the obtained equilibrium lattice constants are found to be in good agreement with the experimental values and other theoretical findings [44]. It was found that the lattice parameters of perovskites increase obviously when X part changes from Br to I, but decrease slightly when B part changes from Sn to Pb. The fitting helps to obtain the physical parameters such as bulk modulus, equilibrium unit cell volume, and the pressure derivatives of the bulk modulus. Comparison of the calculated values of lattice constant, bulk modulus, equilibrium unit cell volume, and pressure derivatives of bulk modulus with experimental and previous theoretical results is shown in Table 1.  

**Band Structure Calculation**  
In this current study, the K-path go from \(\Gamma\) to X to M to \(\Gamma\) to R to X to M and finally to R in the Brillouin zone. The fermi energies were 3.54 eV, 3.03 eV, 1.98 eV and 2.82 eV for MALI, MATI, MALB and MATB respectively. All the considered perovskites have direct band gap. The highest occupied and lowest unoccupied states are at the same high-symmetry k-point, \(\mathbf{R}\). Also, the calculated electronic band gap of the optimized MALB is found to be 1.29 eV, which is not far from the reported experimental value of 1.55 eV [45]. There is a gradual increase in the band gaps when iodine is changed to bromine and found to be 2.01 eV and from 0.59 eV to 1.16 eV for MATI and MATB respectively. The band gaps of MATI is found to be the lowest which further supports the argument that MATI could be the best replacement for MALI.
Fig. 3. Orbital contributions to the band structures of (a) MALI, (b) MATI, (c) MALB and (d) MATB cubic Pm\textbar m phase

4. Conclusion

Summarily, the calculation of sputtering characteristics of the selected perovskites using TRIM, and also the structural and electronic properties calculations of these selected perovskites using density functional theory has been done. From the sputtering characteristics results in our studies, we found the sputtering results of lead perovskite and its best substitute so far, tin perovskite, to be very similar. The sputtering results also indicated a correspondence between sputtering characteristics and PCEs. From the first principles DFT calculations to study structural and electronic properties of selected materials, the optimized equilibrium lattice constant of MALI and MATI in Cubic which are in good agreement with other experimental results. However, the lattice constant of MALB and MATB are a bit larger than the experimental value reported. We discovered that cubic Pm\textbar 3mCH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} gave a band gap result that is close to experimental value reported in this work. Also, CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} and CH\textsubscript{3}NH\textsubscript{3}SnI\textsubscript{3} gave lower band gaps compared to CH\textsubscript{3}NH\textsubscript{3}PbBr\textsubscript{3} and CH\textsubscript{3}NH\textsubscript{3}SnBr\textsubscript{3}. This depicts that CH\textsubscript{3}NH\textsubscript{3}SnI\textsubscript{3} and CH\textsubscript{3}NH\textsubscript{3}SnBr\textsubscript{3} will be a better replacement of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} and CH\textsubscript{3}NH\textsubscript{3}PbBr\textsubscript{3}.

Acknowledgement

The authors of this work will like to acknowledge Covenant University Centre for Research, Innovation and Discovery (CUCRID) for research support.
References

[1] R. Namitha & D. Radhika. Multiwalled Carbon nanotubes for Electrochemical hydrogen storage applications. Journal of Research, Analysis & Development. II, (II). 01-18 2017

[2] N. Noel, S. Stranks, A. Abate, C. Wehrenfennig, S. Guamera, A. Haghhighrad, A. Sadhanala, G. Eperon, S. Pathak, M. Johnston, A. Pertozza, L. Herz, and H. Snaith, Energy Environ. Sci., vol. 7, pp. 3061, 2014.

[3] D. Zhou, Z. Tiantian, T. Yu, Z. Xiaolong and T. Yafang. Perovskite-Based Solar Cells: Materials, Methods, and Future Perspectives. Journal of Nanomaterials 72, 15 2018.

[4] NREL efficiency chart, 2020

[5] A. Babayigit, A. Ethirajan, M. Muller, B. Conings, Toxicity of organometal halide perovskite solar cells. Nat. Mater. 15, 247–251. Benmessaoud et al., 2016;

[6] I. R. Benmessaoud, A. L. Mahul-Mellier, E. Horvath, B. Maco, M. Spina, H. A. Lashuel, and L. Forro, Health hazards of methylammonium lead iodide based perovskites: cytotoxicity studies. Toxicol. Res. (Cambridge, U. K.) 2016, 5, 407–419. 2016.

[7] T. Krishnamoorthy, H. Ding, C. Yan, W. Leong, T. Baikie, Z. Zhang, M. Sherburne, S. Li, M. N. Asta, and S. Mhaisalkar, J Mater Chem., vol. A3, pp. 23829, 2015.

[8] X. Cui, K. Jiang, J. Zhang, M. Su, L. Yang, Y.-L. Song, X.-Q. Zhou, and M. Synth, vol. 209, pp. 247, 2015.

[9] D. Sabba, H.K. Mulmudi, R. R. Prabhakar, T. Krishnamoorthy, T. Baikie, P. P. Boix, S. Mhaisalkar, N. Mathews. Impact of Anionic Br− Substitution on Open Circuit Voltage in Self-organized nanopatterning of silicon surfaces by ion beam sputtering. Materials Science and Engineering R,” Nuclear Inst, and Methods in Physics Research B, vol. 86, pp. 1-44. 2014

[10] J. H. Lee, C.R. Lee, J. W. Park and S. W., (2011) 6.5% efficient perovskite quantum-dot-sensitized solar cell. Nanoscale, 3, 4088-4093.

[11] B. Park, B. Philippe, X. Zhang, H. Rensmo, G. Boschloo, and E. Johansson, Adv. Mater, vol. 27, pp. 6806, 2015.

[12] P. Harikesh, H. Mulmudi, B. Ghosh, T. Goh, Y. Teng, K. Thirumal, M. Lockrey, K. Weber, T. Koh, S. Li, S. Mhaisalkar, and N. Mathews, Chem. Mater., vol. 28, pp. 7496, 2016.

[13] S. Hoefler, G. Trimmel, and T. Rath, “Progress on lead-free metal halide perovskites for photovoltaic applications: a review,” Monatsh Chem., vol. 148, pp. 795, 2017.

[14] O. E. Oyewande & A. Akinpelu. An ion-beam surface sputtering approach to the quest for lead-free metal halide perovskite for solar cells Nuclear Inst. and Methods in Physics Research B 434 102–108 2018.

[15] Watanabe, Eguchi, Yamada & Saito 2015

[16] I. Raifuku, Y. Ishikawa, T. Bourgeteau, Y. Bonnassieux, P. Cabarrocas, and Y. Uraoka, (2010) Instrum. Meth. Phys. Res. B, 268, 1818-1823

[17] E. Oyewande, R. Kree, and A. Hartmann, “Morphological regions and oblique-incidence dot formation in a model of surface sputtering,” Phys. Rev B., vol. 75, pp. 115434, 2006.

[18] M. o.-G. Javier, V. z. Luis, C. Mario, l. G. Rau´, s. R.-C. Andre, M.-B. Ana, and C. Rodolfo, “Self-organized nanopatterning of silicon surfaces by ion beam sputtering. Materials Science and Engineering R,” Nuclear Inst, and Methods in Physics Research B, vol. 86, pp. 1-44, 2014.

[19] E. Oyewande, R. Kree, and A. Hartmann, “Numerical analysis of quantum dots on off-normal incidence ion sputtered surfaces,” Phys. Rev. B, vol. 75, pp. 155325, 2007
[20] R. Kree, A. Hartmann, Geyer, and M. Kolbel, “Long-time effects in a simulation model of sputter erosion,” Phys. Rev. B, vol. 65, pp. 193403, 2002
[21] O. Oyewande, “A unified spatio-temporal framework of the Cuerno-Barabasi stochastic continuum model of surface sputtering,” Commun. Theor. Phys., vol. 58, pp. 165-170, 2012.
[22] O. E. Oyewande, R. Kree, and A. Hartmann. Morphological regions and oblique-incidence dot formation in a model of surface sputtering, Phys. Rev B. 75 115434. 2006
[23] M. C. José, F. Vr, E. A, and F. C. M, “Perovskite thin film synthesised from sputtered lead sulphide,” Scientific Reports vol. 8, pp. 1563, 2018.
[24] M. Gunay. Assessment of the nuetronic performance in some alternative fluids in a fusion-fission hybrid reactor by using monte carlo method. Annals of Nuclear Energy, 60:93–97. 2013
[25] H. Hofsass, K. Zhang, and A. Mutzke, “Simulation of ion beam sputtering with SDTrimSP, TRIDYN and SRIM,” Appl. Surf. Sci., vol. 310, pp. 134-141, 2014.
[26] W. Moeller, and TRI3DYN, “Collisional computer simulation of the dynamic evolution of 3-dimensional nanostructures under ion irradiation,” Nucl. Instrum. Meth. Phys. Res. B, vol. 322, pp. 23-33, 2014.
[27] J. Ziegler, M. Ziegler, and J. Biersack, “The stopping and range of ions in matter,” Nucl. Instrum. Meth. Phys. Res. B, vol. 268, pp. 1818-1823, 2010.
[28] P. Giannozzi, B. Stefano, B. Nicola, C. Matteo, C. C. Roberto, …D. Ceresoli D, et al., QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. Journal of Physics: Condensed Matter, 21, 39. 2009
[29] M. Pazoki, T. J. Jacobsson, A. Hagfeldt, G. Boschloo & T. Edvinsson, Effect of Metal Cation Replacement on the Electronic Structure of Metal Organic Halide Perovskites: Replacement of Lead with Alkaline-Earth Metals. Phys. Rev. B, 93, 144105. 2016
[30] M. Shirayama, H. Kadowaki, T. Miyadera, T. Sugita, M. Tamakoshi, M. Kato, T. Fujiseki, D. Murata, S. Hara, T. N. Murakami, et al. Optical Transitions in Hybrid Perovskite Solar Cells: Ellipsometry, Density Functional Theory, and Quantum Efficiency Analyses for CH3NH3PbI3. Phys. Rev. Appl. 2016, 5, 014012. 2016.
[31] S. Nagane, D. Ghosh, R. L. Hoye, B. Zhao, S. Ahmad, A. B. Walker, M. S. Islam, S. Ogale, A. Sadhanala. Lead-Free Perovskite Semiconductors Based on Germanium–Tin Solid Solutions: Structural and Optoelectronic Properties. J. Phys. Chem. C. 8, 122, 5940–5947. 2018.
[32] R. Mayengbam, S. Tripathy, and G. Palai. First Principle Insights of Electronic and Optical properties of Cubic Organic- Inorganic MAGexPb(1-x)I3 Perovskites for Photovoltaic Applications. J. Phys. Chem. C, 1(18). 2019
[33] W.J.Yin, J. H. Yang, J. Kang, Y. Yan, S. H. Wei. Halide perovskite materials for solar cells: a theoretical review. J. Mater. Chem. A 2015, 3, 8926-8942. 34.
[34] N. Hernández-Haro, J. Ortega-Castro, Y. B. Martynov, R. G. Nazmitdinov, A. Frontera. DFT prediction of band gap in organic-inorganic metal halide perovskites: An exchange-correlation functional benchmark study. Chem. Phys. 2019, 516, 225-231. 2019
[35] J. P Perdew, K. Burke, & M. Ernzerhof, Generalized Gradient Approximation Made Simple. (3), 3865–3868. Pergamon, 1985
[36] T. H. Fischer, & J. Almlöf, General methods for geometry and wave function optimization. Journal of Physical Chemistry, 96(24), 9768–9774. 1992.
[37] P. Khuong, W. Shunnian N. Tien, S. David, F. Zhen, S. Michael, & D. Cuong. Multi Band Gap electronic structure in CH3NH3pbI3. Scientific RepoRts. 9 (21) 44 2019.

[38] W. Yonggang, L. Xujie, Y. Wenge, W. Ting, Y. Liuxiang, R. Xiangting, W. Lin, L. Zheshuai, and Z. Yusheng. Pressure-Induced Phase Transformation, Reversible Amorphization, and Anomalous Visible Light Response in Organolead Bromide Perovskite J. Am. Chem. Soc. 2015

[39] P.E Blöchl. Projector augmented-wave method. Phys. Rev. B Condens. Matter Mater. Phys. 50 17953–17979. 1994

[40] F. D. Murnaghan. (1944). The compressibility of media under extreme pressures, Proceedings of the National Academy of Sciences of the United States of America, 30(9), 244 - 247.

[41] F. Birch. Finite elastic strain of cubic crystals, Physical Review, 71 (11), 809 - 824. Shiferaw Kuma and Menberu Mengesha Woldemariam . Structural, Electronic, Lattice Dynamic, and Elastic Properties of SnTiO3 and PbTiO3 Using Density Functional Theory. Advances in Condensed Matter Physics, 12 1947. 2019

[42] T. Baikie et al., J. Mater. Chem. A, 1 5628. 2013

[43] J. Qian, B. Xu, & W. Tian. A comprehensive theoretical study of halide perovskites ABX 3. Organic Electronics, 37, 61–73. 2016

[44] K. Shiferaw and M. W. Mengesha. Structural, Electronic, Lattice Dynamic, and Elastic Properties of SnTiO3 and PbTiO3 Using Density Functional Theory. Advances in Condensed Matter Physics, 12. 2019

[45] H. Feng, C. Constantinos, P. Robert, and Mercouri G. Anomalous Band Gap Behavior in Mixed Sn and Pb Perovskites Enables Broadening of Absorption Spectrum in Solar Cells. Journal of the American Chemical Society, 136(22), 8094–8099. 2014.