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The Study of Electronic Properties of Perovskite with Methylammonium and Caesium Cation using Density Functional Theory Relativistic

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ABSTRACT

Perovskite has developed as a photovoltaic material. Its power conversion energy has reached 22,1%. One of the perovskite materials was perovskite with methylammonium cation. But, the material has low thermal stabilization, so it needs to evolve by switching cations like cesium. Hence, further research is necessary to compare the electronic structure of both perovskite material to understand how efficiency increase by changing its cation using computational material methods. The computation was done using the ab-initio method with Density Functional Theory (DFT) formulation, Generalized-Gradient Approximation (GGA) as XC functional, and electron-ion core interaction modeled by pseudopotential (PP) relativistic data. The computational results show that MAPbI3 and CsPbI3 have direct band gaps of 1,64 eV and 1,46 eV. The cation switching from MA to Cs has decreased band gap value and generated electron-hole couples, represented by the curvature of the density of states (DOS).

Kata Kunci:

Perovskite
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Cesium
Relativistic

ABSTRAK

Material perovskite telah berhasil dikembangkan menjadi material photovoltaic dan berhasil mencapai efisiensi dalam konversi energi sebesar 22,1%. Salah satu jenis perovskite yang dikembangkan yaitu perovskite dengan kation methylammonium. Tetapi, material tersebut memiliki kestabilan termal yang kurang baik sehingga perlu dikembangkan dengan mengganti jenis kation yang dapat meningkatkan kestabilan termalnya seperti cesium. Oleh karena itu, perlu penelitian lanjut untuk membandingkan struktur elektronik kedua material tersebut agar dapat terlihat seberapa besar peningkatan efisiensi material perovskite terhadap penggantian kationnya melalui metode komputasi material. Pendekatan yang digunakan adalah pendekatan ab-initio, melalui perumusan teori fungsional kerapatan (DFT) dengan pendekatan gradien digeneralisasi (GGA) sebagai fungsional XC serta interaksi elektron dengan inti dimodelkan melalui pendekatan potensial semu dengan data relativistik. Hasilnya, nilai sela energi dari MAPbI3 dan CsPbI3 berturut-turut sebesar 1,64 eV dan 1.46 eV dan penggantian kation MA menjadi Cs berakibat penurunan pada nilai sela energi serta menghasilkan lebih banyak pasangan elektron-lubang dilihat dari kurva rapat keadaan

1. INTRODUCTION

Solar energy is one of the alternative energy sources that are abundant, good environmentally, and was successfully applied in many industrial sectors and household needs. Hence, further research needed to be done to obtain higher power conversion energy and better thermal stability than before. These steps can be done by choosing the right material for a solar cell that functions to convert solar radiation to be electrical energy. Choosing the right material can be seen from its thermal stabilization and electronic properties.

Perovskite is a semiconductor material that structure is ABX_3 (A=cation, B=metal, C=halide ion). This material has a high coefficient absorption, wide range spectrum, a high mobility carrier, and long diffusion length (Kim, 2012). Since its first application, perovskite has efficiency 3,8% and grow until now, reached 22,1%, so perovskite to be photovoltaic material has efficiency get near to silicon with low-cost production (Zhang, et al, 2016). Developing perovskite material such as perovskite with methylammonium cation and perovskite with cesium cation. Kulbak (2016) showed that perovskite with cesium cation is thermally stable compared to methylammonium cation for two weeks. Therefore, this research proposed to compare both perovskite materials from its electronic properties.

The way for identify electronic properties of material could be used with computation method that constructing ab-initio model from Schrodinger equation. But, it could not be solved analytically for many electron cases, so numerical calculation approach must be used that was Density Functional Theory (DFT) formulation. DFT provide a balance between accuracy and complexity of calculation (Gygi and Giulia, 2005). DFT used approximation of electron-electron and electron-nuclear interaction that was Generalized Gradient Approximation (GGA) and Pseudopotential. Selecting pseudopotential was depended on type of atom in perovskite material, in that case Pb atom. Pb has greater mass than other atom in the perovskite, so relativistic effect should be not ignored in pseudopotential for better result. Relativistic effects were treated as one of the parameters in producing the accuracy of a calculation. The result of DFT calculation was electronic properties that was energy band and Density of States (DOS) in ground state.

2. METODE PENELITIAN

The study was conducted by material computation method via ABINIT version 8.10.3 software providing many numerical and physical approached to modeling material properties. Material Modeling used first-principle calculation or ab-initio method with numerical method from the Schrodinger equation based density functional theory. The result included total energy, band energy structure, and density of states which was implemented in Abinit code (Gonze et al., 2009 and Gonze et al., 2016). Generalized-Gradient Approximation (GGA) as functional of exchange-correlation (XC) and interaction between electron-core was modeled by the pseudopotential with relativistic data.

2.1. *Crystal Structure Optimization*

This step aims to obtain optimal crystal structure as shown by minimum total energy which was obtained. Optimization divided into two stages. The first stage intends to correct the atomic positions in its unit cell. Second stage head to repairing geometry from the unit cell like lattice parameter and angle lattice vector. Each geometry structure was optimized with a cutoff energy and Brillioun zone was sampled with 6x6x6 Monkhorst k-points. The convergence limit of 1×10^{-10} Ha/unit cell for total energy and $1x10^{-5}$ Ha/Bohr for maximum force.

2.2. *Calculation of Electronic Properties*

Crystal structure which was optimized would be input data for the density of states and band energy calculation. Structure of energy band was calculated each k point in the first brilliant zone. Density of states and energy band structure was plotted by XMGRACE software. Then, from graph of energy band could be seen direct gaps from the difference between the energy of conduction band

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minimum and valence band maximum at same k-point. While, indirect gaps were determined from the difference between the energy of conduction band minimum and valence band maximum at different k-point.

3. RESULT AND DISCUSSION

3.1. *CsPbI3*

The result of optimization shows that CsPbI3 stable structure was cubic (Fig.1) which was signed by angle of lattice constantly in 90o. When optimizing, lattice constant was changed about 0.3% smaller than first structure, so unit cell volume was shrinked 0.9%.

Figure 1 shows atomic bonds in $CsPbI_3$ perovskite. Pb atom was binding all I atom (6 atoms) in its around and Cs atom was filling space between Pb-I bonds. The unit cell consists 1 Cs, 1 Pb, and 3 I atoms. Lattice constant which was obtained from GGA-Relativistic, experiment, and other ab-initio indicate the difference what depends by parameters what used at the time of calculation.

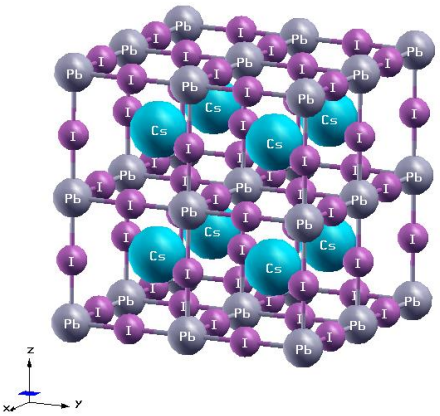

Figure 1. Structure of $CsPbI_3$

From Table 1, the difference in lattice constant was caused by using different physical and numerical approaches. For Møller's experimental case, it was found that the $CsPbI_3$ structure was monoclinic, while Trots produced a cubic structure. The difference in structure is at the temperature used. Møller found the structure at a temperature of 308°C while Trots was at 343°C so it could be concluded that the structure could be modified experimentally depending on the temperature applied. Another case for ab-initio calculations, different parameters lied in the physical approach such as the pseudopotential used and also the numerical approach such as the cut-off kinetic energy, k point integration, and the optimization logarithm used. From the data, the difference ranges from 3-6% between the calculations in this study and other ab-initio calculations, whereas when compared to experimental data, it shifted about 1 - 3%.

Table 1. Comparison of the lattice constant (Å) $CsPbI_3$ with experimental data and other ab-initio calculations with different approaches

Konstanta Kisi	GGA Relativistik	Exp 1[*)]	Exp 2[#)]	*ab-initio* lainnya	
				LDA[$)]	FP-LAPW + GGA[^)]
a	6,395 Å	6,15 Å	6,29 Å	6,05 Å	6,18 Å
b	6,395 Å	6,15 Å	6,29 Å	6,05 Å	6,18 Å
c	6,395 Å	6,23 Å	6,29 Å	6,05 Å	6,18 Å

[*)] Filip, dkk (2014), [#)] Chang dan Park (2004), [$)] Murtaza dan Iftikhar (2011), [^)] Sun dan Zhang (2019)

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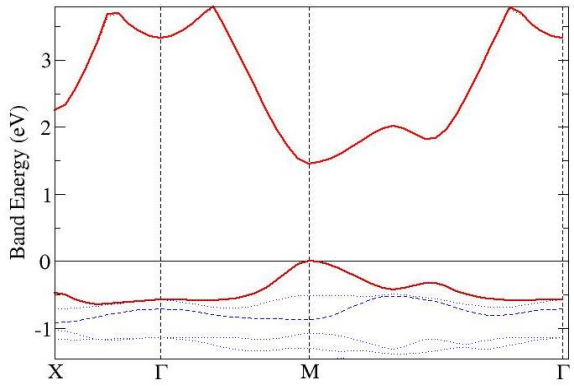
After the crystal structure has been optimized, the energy as a function of electron waves vector in the crystal, that is k-point in first Brillioun Zone, was plotted into the energy band structure.



In the $CsPbI_3$ material with the XC GGA functional and relativistic calculation, the direct energy gap is 1.456 eV. Direct gaps were located at point k at point M (0.5; 0.5; 0) (Figure 2).

Figure 2: Energy band structure of $CsPbI_3$

In table 2, the calculations performed have a relative difference of ~ 15.8% to the energy gap obtained from the experiment. Experiments were carried out by maintaining a $CsPbI_3$ temperature of around 400°C which resulted in a perovskite structure (Filip, 2014). The difference in the energy gap between the DFT calculation process and the experiment was because the DFT calculation only uses the wave function in the ground state, which in reality involves an excitation state with a higher energy that will be more effective in determining the intervals of energy, therefore the results DFT would be lower than the experimental value (Afsari, 2016) depending on the approach used again.

Table 2: Comparison of the energy gaps of each method in $CsPbI_3$

Method	Energy Gaps (eV)
GGA-Relativistik	1,456
Eksp. *)	1,73
LDA#)	1,11
FP-LAPW + GGA$)	1,3
GGA + PBE^)	1,483

*) *Filip, dkk (2014),* #) *Chang dan Park (2004),* $) *Murtaza dan Iftikhar (2011),* ^) *Sun dan Zhang (2019)*

3.2. *$MAPbI_3$*

The process of optimizing the crystal structure resulted in a new lattice constant which experienced a relative shrinkage of 0.4% - 0.65%. This perovskite has pseudocubic crystal structure in a stable state. It was called pseudocubic because the value between the lattice constants has a difference of only 0.01 Å so that the structure looks as if it is cubic in shape (Stoumpus, 2013). In Figure 3, the atoms that act as cations in the cubic center are seen in $MAPbI_3$ carbon atoms (C), nitrogen (N), and hydrogen (H) which form bonds in methylammonium (MA) compounds.

Based on the data in Table 3, the lattice constant obtained from the relativistic DFT-GGA calculation was the lowest lattice constant value compared to ab-initio with a different approach. The percentage difference relative to the experiments conducted by Oku was 2.1-2.27% lower, while the Stoumpus experiment was 0.87-1.06% lower as well. The conclusion from these data is obtained using relativistic GGA, the structure formed at the lowest energy is in the form of an orthorhombic crystal system which is different from the experiment, namely cubic which is synthesized at a

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temperature of 330 K (Oku, 2015) and tetragonal or pseudocubic at a temperature of 400 K (Stoumpus, 2013).

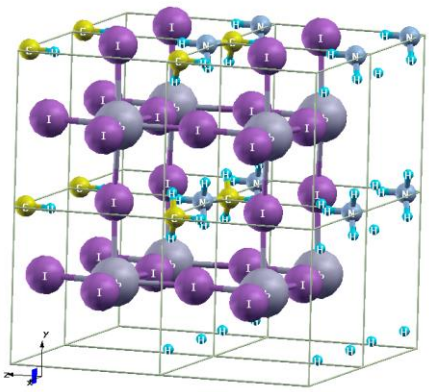

Figure 3. Structure of $MAPbI_3$

The energy band structure of $MAPbI_3$ was divided into 4 segments with 5 k points that are selected symmetrically in the first Brillioun Zone. The fermi energy is set at 0 eV as a reference point to find the energy gap. In Figure 4, The red lines represent the valence band maximum (VBM) and the conduction band minimum (CBM). Direct gaps were located at point M with an energy gap value was 1.64 eV and an indirect gaps was 1.58 eV.

Table 3. Comparison of the lattice constant (Å) $MAPbI_3$ with experimental data and other ab-initio calculations with different approaches

Konstanta Kisi	GGA Relativistik	Exp. 1*)	Exp. 2#)	*ab-initio* lainnya	
				GGA$)	PBEsol^)
a	6,256 Å	6,391 Å	6,311 Å	6,332 Å	6,29 Å
b	6,249 Å	6,391 Å	6,311 Å	6,332 Å	6,23 Å
c	6,249 Å	6,391 Å	6,316 Å	6,332 Å	6,37 Å

**) Oku (2015) | #) Stoumpus, dkk (2013) | $) Amnuyswat dan Thanomngam (2017) | ^) Brivio, dkk (2015)*

Based on Table 4, the relative difference each energy gap was found to be 5.8% between the Relativistic-GGA calculation and the experiment. Like the $CsPbI_3$ material, the DFT with the GGA function and the relativistic pseudopotential used is still not effective in determining the energy gap value accurately, therefore it is necessary to correct the inter-energy value.

Table 4. Comparison of the energy gaps of each method in $CsPbI_3$

Method	Energy Gaps (eV)
GGA-Relativistik	1,64
Exp. *)	1,55
SOC + GW#)	1,67
GGA + PBE^)	1,3

*) Oku (2015), #) Stoumpus, dkk (2013), ^) Brivio, dkk (2015)

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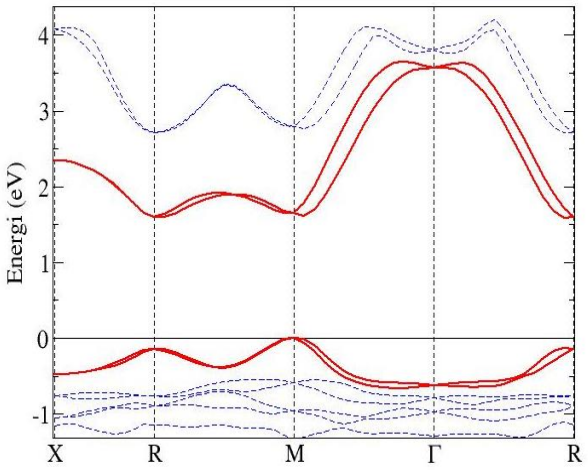

Figure 4. Energy band structure of $MAPbI_3$

3.3. *$MAPbI_3$*

The $CsPbI_3$ and $MAPbI_3$ materials involve Pb atoms as metal ions in the perovskite structure. The atom Pb has a very heavy mass when compared to the mass of electrons or holes. This needs to involve a relativistic effect because of the huge difference in mass. In the end, this results in a difference in the inter-energy value of the material.

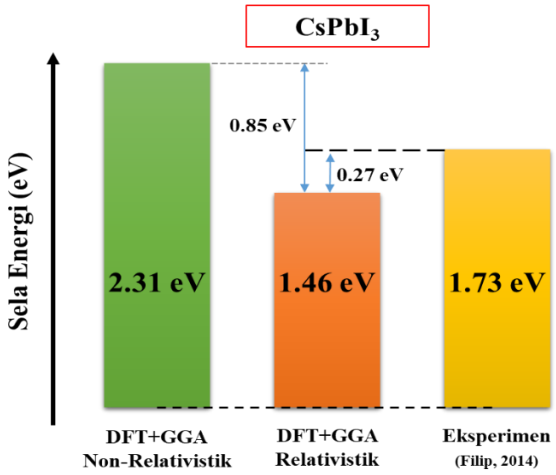

Figure 5. Energy gap of $CsPbI_3$ with relativistic, non-relativistic effects, and experimental.

Based on the graph for $CsPbI_3$ (Figure 5), the energy gaps value obtained from non-relativistic and full-relativistic calculations is 2.31 eV and 1.46 eV which have a relative difference of 36.7%. When compared with experimental data, non-relativistic calculations have a higher difference between the energy intervals of 0.58 eV and lower relativistic calculations with a difference of 0.27 eV. From these data calculations involving relativistic effects can describe the energy gap value that is almost closer to experimental data than non-relativistic calculations.

The same thing happened to MAPbI3 (Figure 6), that the calculation involving the relativistic effect can calculate the energy gap value that is closer to the energy gap value generated from the experimental process. The difference in the results from non-relativistic reaching 0.82 eV is considered very large when compared to the difference between the relativistic results and the experiment which is only 0.09 eV. Therefore, it can be concluded that the calculation using the relativistic effect also succeeded in obtaining an energy gap value that was close to the experimental data based on the two materials tested, namely $CsPbI_3$ and $MAPbI_3$.

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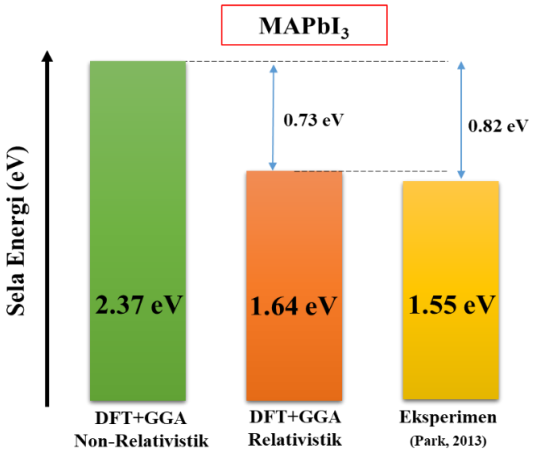

Figure 6. Energy gap of $MAPbI_3$ with relativistic, non-relativistic effects, and experimental.

3.4. *Cation Replacement Effect*

$MAPbI_3$ and $CsPbI_3$ belong to the same group, namely perovskite material which has a chance as photovoltaic material in solar panels based on the score of the energy gap. Perovskite that has been developed is a cation in the form of Methylammonium Perovskite (MAP) such as $CH_3NH_3PbBr_3$ and Cesium (Cs) based cations such as CsPbBr3, which shows that Cs-based perovskite is more stable in thermal properties than MAP-based under conditions of use for 2 weeks (Kulbak, 2016). Therefore, the cationic element in perovskite material affects the stability and lifetime of the material. In this study, the effect of perovskite cation substitution from MA to Cs was seen in the enegy band structure and state density.

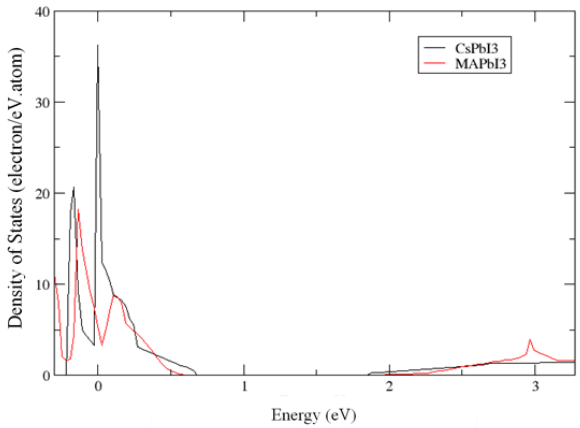

Figure 7. Density of States for $CsPbI_3$ and $MAPbI_3$ using of DFT + GGA Relativistic

The density of states that is displayed in Figure 7 can provide information that there is an energy gap because the region has no state for electrons to occupy in that energy range. The absence of a state translates to a forbidden energy region in the energy band structure. The number of states near the fermi energy can indicate the number of electron-hole pairs that will form when the energy from the wave exceeds that of the energy gap. The more electron-hole pairs will affect the amount of current density generated into electrical energy. Substitution of perovskite cations from MA cations to Cs or vice versa directly affects the width of the energy gap. The effect of changing MA to Cs is to increase the energy of the maximum valence band by ~ 0.08 eV and reduce the energy of the minimum conduction band by ~0.07 eV.

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Therefore, changing the MA cation to Cs makes the energy gap smaller by ~0.15 eV. When viewed in terms of efficiency as a photovoltaic material, the replacement of MA cations to Cs will result in an increase in the value of efficiency. Based on the Shockey-Queiesser limit curve, the efficiency value obtained by $MAPbI_3$ is around ~30.14%, whereas if cation replacement is done, the efficiency of $CsPbI_3$ becomes ~32.91%.

4. CONCLUSION

The conclusion obtained from this study is that the optimal crystal structure for $CsPbI_3$ is cubic perovskite while $MAPbI_3$ has an orthorhombic/pseudocubic perovskite structure. The energy gap resulting from the calculation of the relativistic DFT + GGA is 1.46 eV for $CsPbI_3$ and 1.64 eV for $MAPbI_3$. The relativistic effect on the calculation gives the energy gap value closer to the experimental data by 30-37% compared to non-relativistic based on the tested materials, namely $CsPbI_3$ and $MAPbI_3$. The effect of changing MA cations to Cs only resulted in decreasing the energy gap by about ~ 0.15 eV which contributed to the change in efficiency from ~ 30.14% to ~ 32.91% based on Shockley-Queisser Limit.

REFERENSI

[1] Afsari, M., Boochani, A., dan Hantehzadeh, M. (2016), 'Electronic, Optical and Elastic Properties of Cubic Perovskite $CsPbI_3$: using First Principles Study', *Optik,* Vol. 127, No.23, hal. 11433-11443.

[2] Amnuyswat, K., dan Thanomngam, P. (2017), 'Effect of exchange-correlation and GW approximations on electrical property of cubic, tetragonal and orthorhombic $CH_3NH_3PbI_3$', *Integrated Ferroelectrics,* Vol. 177, No.1, hal. 1-9.

[3] Brivio, F., Frost, J. M., Skelton, J. M., Jackson, A. J., Weber, O. J., Weller, M. T., dan Walsh, A. (2015), 'Lattice Dynamics and Vibrational Spectra of the Orthorhombic, Tetragonal, and Cubic Phases of Methylammonium Lead Iodide', *Physical Review B,* Vol. 92, No.14, hal. 144308.

[4] Chang, Y. H., dan Park, C. H. (2004), 'First-Principles Study of the Structural and the Electronic Properties of the Lead-Halide-Based Inorganic-Organic Perovskites $(CH_3NH_3)PbX_3$ and $CsPbX_3$ (X = Cl, Br, I)', *Journal of the Korean Physical Society,* Vol. 44, No.4, hal. 889-893.

[5] Filip, M. R., Eperon, G. E., Snaith, H. J., dan Giustiono, F. (2014), 'Steric engineering of metal-halide perovskites with tunable optical band gaps', *Nature Communications,* Vol. 5, hal. 5757.

[6] Gonze, X., Amadon, B., Anglade, P.-M., Beuken, J.-M., Bottin, F., P., B., Bruneval, F., dkk. (2009), 'ABINIT : First-principles Approach of Materials and Nanosystem Properties', *Computer Physics Communication,* Vol. 180, hal. 2582-2615.

[7] Gonze, X., Jollet, F., Araujo, F. A., Adams, D., Amadon, B., Applencourt, T., dan Geneste, G. (2016), 'Recent Developments in the ABINIT Software Package', *Computer Physics Communication,* Vol. 205, hal. 106-131.

[8] Gygi, F. & Giulia, G. (2005), 'Ab Initio Simulation in Extreme Conditions'. *Materials Today*, hal. 26-27.

[9] Kim, H., Kim, U., Kim, M. H., Kim, T. H., Mun, H. S., Jeon, B. G., dan Char, K. (2012), 'High Mobility in a Stable Transparent Perovskite Oxide', *Applied Physics Express,* Vol. 5, hal. 061102.

[10] Kulbak, M., Gupta, S., Kedem, N., Levine, I., Bendikov, T., dan Hodes, G. (2016), 'Cesium Enhances Long-Term Stability of Lead Bromide Perovskite-Based Solar Cells', *Journal of Physical Chemistry Letter,* Vol. 7, hal. 167-172.

[11] Møller, C. K. (1958), 'Crystal Structure and Photoconductivity of Cæsium Plumbohalides', *Nature,* Vol. 182, hal. 1436.

Submitted December 2022, Revised December 2022, Accepted December 2022, Published December 2022

[12] Murtaza, G., dan Iftikhar, A. (2011), 'First Principle Study of The Structural and Optoelectronic Properties of Cubic Perovskite $CsPbM_3$ (M=Cl, Br, I)'. *Physica B,* Vol. 406, hal. 3222-3229.
[13] Oku, T. (2015), 'Crystal Structures of CH3NH3PbI3 and Related Perovskite Compounds Used for Solar Cells' dalam *Solar Cells: New Approaches and Reviews, eds. L. A. Kosyachenko, InTech, Rijeka*, hal. 77-100.
[14] Stoumpus, C. C., Malliakas, C. D., dan Kanatzidis, M. G. (2013), 'Semiconducting Tin and Lead Iodide Perovskites with Organic Cations: Phase Transitions, High Mobilities, and Near-Infrared Photoluminescent Properties', *Inorganic Chemistry,* Vol. 52, hal. 9019-9038.
[15] Sun, Y., dan Zhang, H. (2019), 'Density Functional Theory Study on the Electrical Properties of alpha-CsPbX3 (X=I, Cl, Br)', *American Scientific Research Journal for Engineering, Technology, and Sciences (ASRJETS),* Vol. 61, No.1, hal. 1-6.
[16] Trots, D., dan Myagkota , S. (2008), 'High-temperature Structural Evolution of Caesium and Rubidium Triiodoplumbates', *Journal of Physics and Chemistry,* Vol. 69, hal. 2520-2526.
[17] Zhang, W., Giles, E., dan Henry, J. (2016), 'Metal Halide Perovskite for Energy Application', *Nature Energy,* Vol. 1, hal. 1-8.

Submitted December 2022, Revised December 2022, Accepted December 2022, Published December 2022