Solid State Science and Technology, Vol. 25, No 1 (2017) 1-8
ISSN 0128-7389 | *http://journal.masshp.net*

CHARACTERIZATION OF ORGANIC-INORGANIC PEROVSKITES BASED ON REACTION OF AMINOMETHYL PYRIDINE

Azliana Ramli, Nur Fairuz Mohd Rostan,
Nafisah Osman and Farhana Othman

Faculty of Applied Sciences,
Universiti Teknologi MARA, 02600 Arau, Perlis, Malaysia.

Corresponding author: aazliana@perlis.uitm.edu.my

ABSTRACT

Different positions of aminomethyl pyridine (AMP) of 2-AMP, 3-AMP and 4-AMP hybrid perovskite were synthesized in this study. The reaction of respective AMP with lead bromide ($PbBr_2$) via reflux process at temperature of 90°C resulted to the yellowish organic- inorganic powder. The synthesized products were characterized using Ultraviolet-Visible Spectroscopy (UV-Vis), Fourier Transform Infrared (FTIR) Spectroscopy and Energy Dispersive X-Ray (EDX). The UV-Vis analysis revealed that the maximum excitation peak in the absorption spectra for different position of AMP were located at 424 nm for 2-AMP, 368 nm for 3-AMP and 359 nm for 4-AMP. As a result, different position of AMP gave significant different values of calculated energy gap of 2.93 eV, 3.37 eV and 3.46 eV for 2-AMP, 3-AMP and 4-AMP, respectively. The chemical bonding of ammonium ion (NH_3^+), pyridinium ion ($C_5H_6N^+$) and aromatic hydrocarbon (Ar-H) at functional group of benzene ring of 2-AMP, 3- AMP and 4-AMP were subsequently observed in the range of 3369 to 3385 cm^{-1} as shown by the FTIR spectrum. The slight shift of the wavenumber in the range of 3369 to 3385 cm^{-1} indicates the electronegative ion of nitrogen atom in the pyridine ring. The EDX analysis showed the elementals composition bromine (Br) and plumbum (Pb) atoms are almost similar in the synthesized AMP products.

Keywords:Hybrid perovskite; aminomethyl pyridine; energy gap

INTRODUCTION

Nowadays, a lot of clean and green technologies have being introduced to reduce the usage of non-renewable energy sources that has been depleted due to the increasing of energy demand. The alternative of renewable energy resources such as solar energy will become another competitive solution to overcome the problems. Solar energy was perhaps the only known renewable-type energy resource for sustainable economic development with minimum detrimental impact on the environment since the sunlight is an abundant and clean source of energy [1,2]. The growing demands for alternative energy in developed countries such as United Sates, China and Japan had sparked the rapid development of solar energy generation. The utilization of solar energy was predicted to become the second important source of energy in the next five years period.

Although crystalline silicon solar cells remain as the dominating photovoltaic (PV) technology worldwide with industrial-scale production, there are other alternatives such as CuInGaSe2-based thin-film solar cells [3], organic bulk junction solar cells [4], dye-sensitized solar cells (DSSCs) [5] and devices based on earth-abundant non-silicon semiconductors like cuprus oxide [6,7] and cupric bromide [8]. Meanwhile, the approach of synthesizing perovskite type solar cell already being carried out since year 2012 and the researchers had shown some interest in producing perovskite structure-based solar cells [9]. The effort in the perovskites- based mesoporous solar cells developments has potential to become low-cost alternative for commercially available solar cell technologies [10]. The technologies of invention in Lead Halide Organic-Inorganic solar cell industry has very high potential based on research made by Park N.G in year 2013. He found that the elevated solid-state based perovskite solar cell has potential to achieve 20% of efficiency under low-cost of productions [2,11].

The most studied semiconducting hybrid are the organic-inorganic perovskite-based structure of ABX_3 (A=organic, B=inorganic and X_3=halide) as light-harvester in solid PV devices [12- 15]. The perovskite-sensitizer was selected as a new potential material in solar cell architecture device due to its low-processing temperature that makes the production of future solar cell become more efficient and cost-effective. In this work, we synthesized and examined the optical properties, functional group and elemental analysis of synthesized products based on the reaction of the different position of aminomethyl pyridine (AMP) with metal-halide in the acidic medium solution. Due to limited studies of the aminomethyl pyridine (AMP) in perovskite- based solar cell as well as less fundamental study on AMP have motivate us to fill this gap of knowledge.

EXPERIMENTAL

Synthesize Compound.

Lead (II) Bromide, $PbBr_2$ (99%, Systerm), 2-(aminomethyl) pyridine (98%, Merck), 3-(aminomethyl) pyridine (98%, Merck) and 4-(aminomehtyl) pyridine (98%, Acros Organics) were used without further purification. Meanwhile, concentrated hydrobromic acid (HBr) (48%, Sigma-Aldrich) was diluted to obtain 10 mL of 40% acid solution by the dilution of 8.3 mL of concentrated HBr acid with 1.7 mL of distilled water.

The compound of respective 2-AMP, 3-AMP and 4-AMP with $PbBr_2$ in HBr solution were synthesized via reflux method, using slow heat until 90°C. The synthesized products were cooled down slowly to room temperature of 28°C. The reaction products formed as small crystal deposition inside the mixture and then filtered to obtain only the solid crystals. The product from the chemical reaction of aminomethyl pyridine (AMP) with lead bromide ($PbBr_2$) in acidic medium of hydrobromic (HBr) acid will have the hybrid characteristics from organic and inorganic materials.

Characterization.

The synthesized compound of respective 2-AMP, 3-AMP and 4-AMP were analyzed to observe the optical and chemical of the hybrid (organic-inorganic)-perovskite properties. The optical properties of the samples were analyzed using Ultra-Violet Visible (UV- Vis) spectrophotometer (Model: Carry 50). The synthesized samples were observed under the UV-Vis spectrophotometer to observe the optical behavior of each AMP compound. Meanwhile, the functional groups of the samples were observed using Fourier Transform Infra- red Spectroscopy (FTIR) analysis (Thermo Electron Corporation Model Nicholet 380) with the KBr pellet technique. The elemental compositions of the crystal formed by different reaction of AMP were investigated using the Scanning Electron Microscope/Energy Dispersive X-Ray (SEM/EDX) (Model Zeiss EVO50) with operating voltage of 20kV.

RESULTS AND DISCUSSION

Eye inspection on the appearance of the synthesized samples seem to be ‘needle-like’ solid crystal. The smaller size of the crystal particles can increase the strength and other optical properties. The absorption wavelength obtained from the UV-Vis revealed that the highest absorption peak, λ_{max} were detected at 424 nm, 368 nm and 359 nm for 2-AMP, 3-AMP compound and 4-AMP compound, respectively. The absorbance spectra against wavelength were plotted as shown in Figure 1.

The experimental values obtained were in agreement with the previous research reported by Li et. al. [3], they quoted that the maximum wavelength, λ_{max} of 2-AMP product was 431 nm. The bandgap energy calculated for 2-AMP, 3-AMP and 4-AMP was determined by the equation (1).

$$E_g = \frac{hc}{\lambda_{\max}} \qquad (1)$$

Where E_g is the optical band gap that determines the portion of the solar spectrum of a photovoltaic cell absorbs.

The calculated values for the energy gap were 2.93 eV, 3.37 eV and 3.46 eV for the 2-AMP, 3-AMP and 4-AMP, respectively. From the value obtained, the bandgap energy of the synthesized compound were increased with the decreasing of the absorption spectra wavelength. Since the product of 4-AMP exhibit the shortest maximum wavelength among the AMP products, therefore it had the highest energy bandgap than others. The larger the contribution of orbital of perovskite yield to larger value of the bandgap energy. Furthermore, the ‘p’orbital of Pb atom in AMP affect the conduction band minimum, while ‘p’ orbital of Br atom influence the valence band maximum [16].

The functional group of amino (NH_3^+), pyridinium and aromatic hydrocarbon (Ar-H) that contained in the different AMP position in the pyridine ring of hybrid perovskite were analyzed and the result obtained from the FTIR analysis were listed in Table 1. The data obtained were then compared to the previous research by Li et. al. [13].

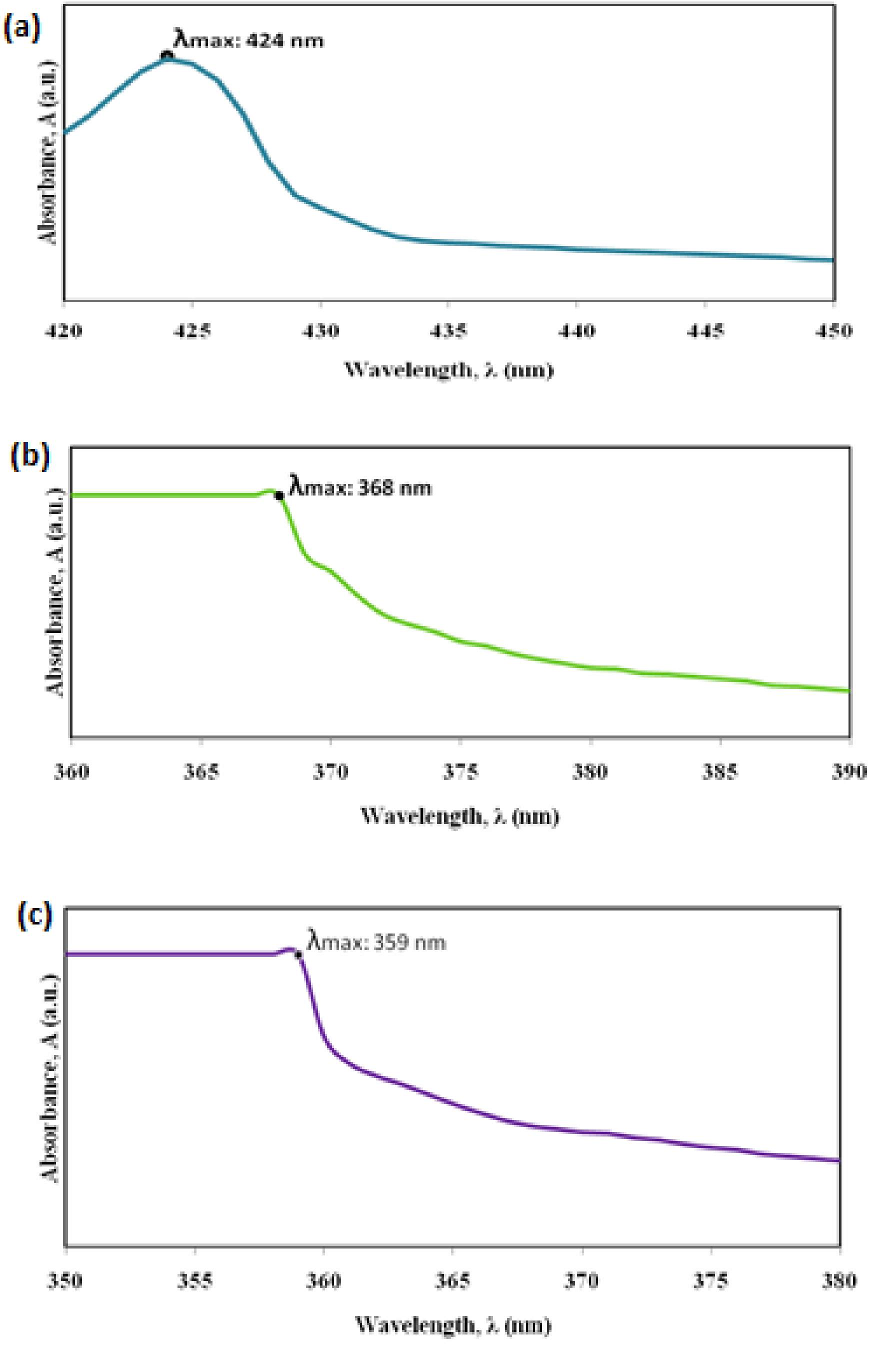
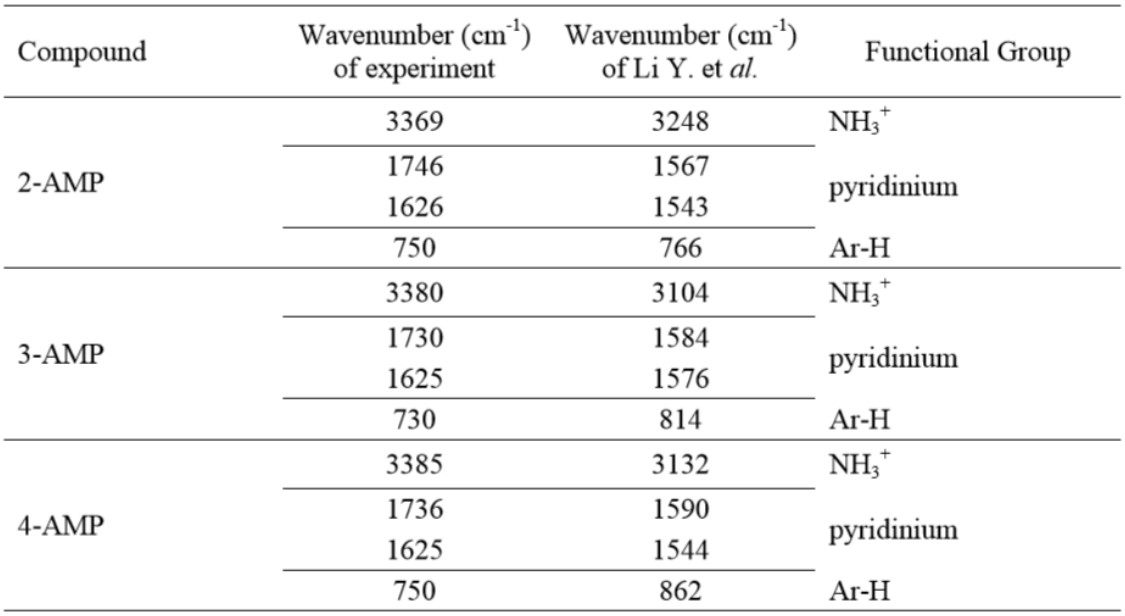


Figure 1: Maximum wavelength, λ_{max} for (a) 2-AMP, (b) 3-AMP and (c) 4-AMP.

Table 1: FTIR band in 2-AMP, 3-AMP and 4-AMP



Compound	Wavenumber (cm^{-1}) of experiment	Wavenumber (cm^{-1}) of Li Y. et *al.*	Functional Group
2-AMP	3369	3248	NH_3^+
	1746	1567	pyridinium
	1626	1543	
	750	766	Ar-H
3-AMP	3380	3104	NH_3^+
	1730	1584	pyridinium
	1625	1576	
	730	814	Ar-H
4-AMP	3385	3132	NH_3^+
	1736	1590	pyridinium
	1625	1544	
	750	862	Ar-H

The chemical bonding of NH_3^+ of the AMP products were observed within the range of 3369 to 3385 cm^{-1} between the 2-AMP to 4-AMP in the pyridine ring. The existence of AMP in three (3) structures can be clearly shown by the bands in the region of 1746 – 1625 cm^{-1} that indicates of the pyridinium group. The absorption bands of the synthesized products prepared under ambient atmosphere were slightly shifted to higher wavelength might be due to the refluxing process was not been done in the nitrogen (N_2) atmosphere as proposed by Li et. al. [13].

EDX analysis was carried out to determine the elemental composition in the compound on the solid surface. In Figure 2, it is clearly shown the existence of Br and Pb atoms in the AMP products. The ratio of Br: Pb atoms were mostly equal to each AMP products since the perovskites produces only different in atomic position of methylamine. The ratio of Br: Pb atoms obtained were denoted in the spectra analysis were $Br_{17.21}Pb_{3.51}$, $Br_{12.37}Pb_{2.32}$, $Br_{13.61}Pb_{2.66}$ for 2-AMP, 3-AMP and 4-AMP products, respectively. From this analysis, it shown that the starting material of aminomethyl pyridine are homogenously distribute with $PbBr_2$ under reflux condition at slow heat of 90°C [17].

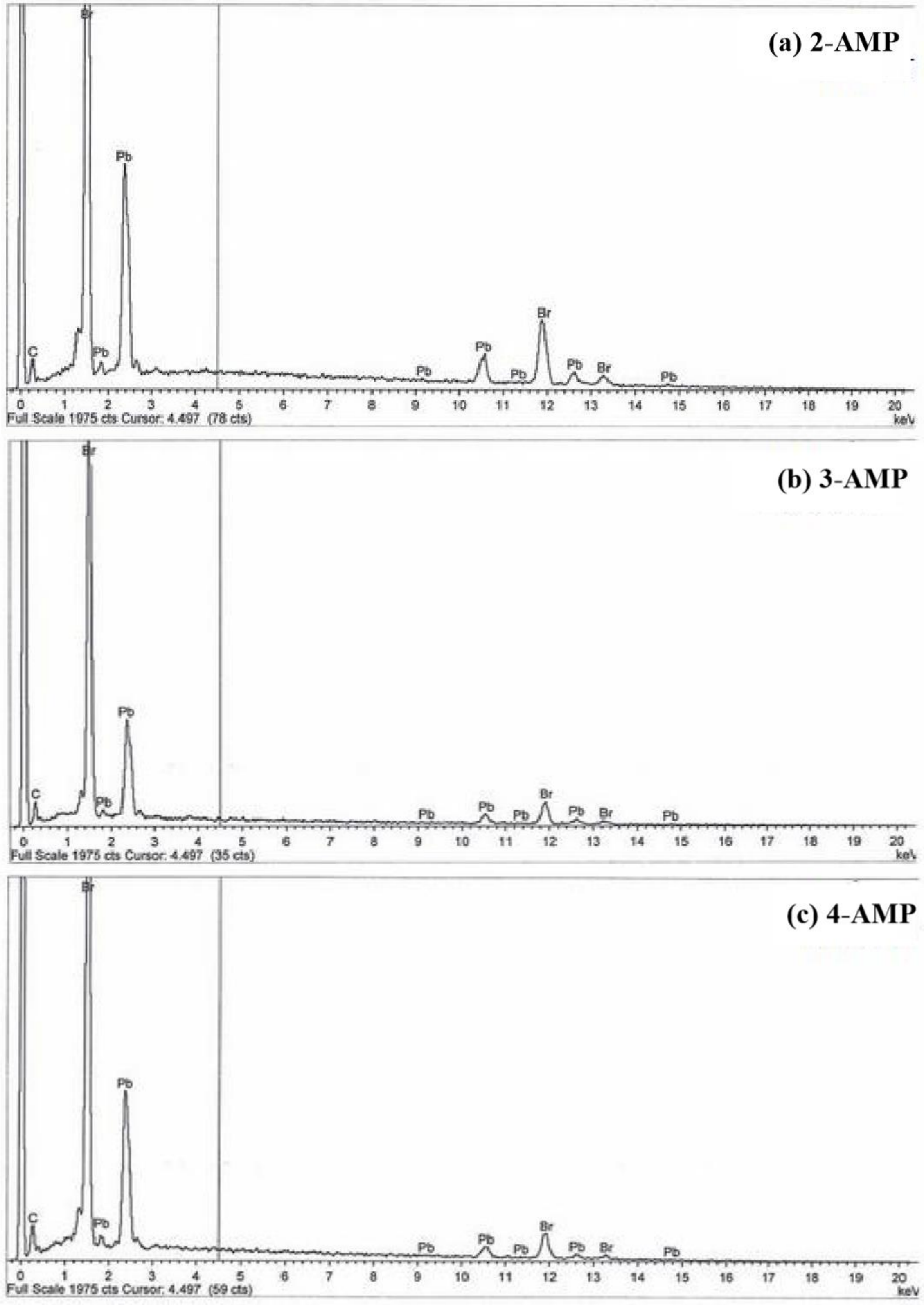


Figure 2: EDX spectra of (a) 2-AMP, (b) 3-AMP and (c) 4-AMP

CONCLUSION

The combination of aminomethyl pyridines (AMP) with lead(II) bromide ($PbBr_2$) were progressively done in 40% hydrobromic acid medium at appropriate condition of 90°C via reflux technique. The optical properties of the synthesized AMP products were successfully determined with UV-Vis. The FTIR spectrum was used to analyze the change in wavenumber of AMP after $PbBr_2$ was incorporated. The slight shift in wavenumber has proved that there was chemical interaction of different position of AMP with the $PbBr_2$. The chemical compositions of different AMP products were observed by the EDX data analysis and proved the existence of Br and Pb elements. Further research in this organic-inorganic halide compound is in progress to reduce the grain size so that it can be applied in mesoscopic solar cell as sensitizers.

ACKNOWLEDGEMENT

The authors thank to the Ministry of Higher Education (MOHE) for the Fundamental Research Grant Scheme (FRGS/2014) and Universiti Teknologi MARA (UiTM) for the facilities and supports.

REFERENCES

[1] M.A. Green, K. Emery, Y. Hiskikawa, W. Warta, E.D. Dunlop, *Prog. Photovoltaics Res. Appl.* **21** 827-837 (2013)
[2] H.J. Snaith, *Journal of Physics Chemistry Lett.* **4** 3623-3630 (2013)
[3] I. Repins, M.A. Contreras, B. Egaas, C. DeHart, J. Scharf, C.L. Perkins, B. To, R. Noufi, *Prog. Photovoltaic Res. Appl.* **16** 235-239 (2008)
[4] R.F. Service, *Science* **332** 293 (2011)
[5] B. O'Regan, M. Gratzel, *Nature* **353** 737-740 (1991)
[6] Z. Zang, A. Nakamura, J. Temmyo, *Opt. Express* **21** 11448-11456 (2013)
[7] S.W. Lee, Y.S. Lee, J. Heo, S.C. Siah, D. Chua, R.E. Brandt, S.B. Kim, J.P. Mailoa, T. Buonassisi, R.G. Gordon, *Advance Energy Materials,* **4** 1301916 (2014)
[8] X.P. Cui, K.J. Jiang, J.H. Huang, Q.Q. Zhang, M.J. Su, L.M. Yang, Y.L. Song and X.Q. Zhou, *Synthetic Metals* **209** 247-250 (2015)
[9] P. P. Boix, K. Nonomura, N. Mathews and S. G. Mhaisalkar, *Materials Today.* **17** 16-23 (2014)
[10] S. Senthilarasu, E.F. Fernandez, F. Almonacid and T.K. Mallick, *Solar Energy Materials & Solar Cells* **133** 92-98 (2015)
[11] N.G. Park, *Journal of Physical Chemistry Letters,* **15** 2423-2429 (2013)
[12] A.D. Sheikh, A. Bera, M.A. Haque, R.B. Rakhi, S.D. Gobbo, H.N. Alshareef and T. Wu, *Solar Energy Materials* **137** 6-14 (2015)
[13] Y. Li, G. Zheng, C. Lin and J. Lin, *Solid State Sciences* **9** 855-861 (2007)
[14] A. Wakayima, M. Endo, T. Ssamori, N. Tokitoh, Y. Ogomi, S. Hayase and Y. Murata, *Chemistry Letters* **43** 711-713 (2014)

[15] B. Tripathi, P. Bhatt, C. Kanth, P. Yadav, B. Desai, M.K. Pandey and M. Kumar, *Solar Energy Materials and Solar Cells* **132** 615- 622 (2015)

[16] Y.Y. Pan, Y.H. Su, C.H. Hsu, L.W. Huang and C.C. Kaun, The electronic structure of organic-inorganic hybrid perovskite solar cell: A first-principles analysis. Computational Materials Science **117** 573-578 (2016)

[17] N. Rezlescu, E. Rezlescu, P.D. Popa, C. Doroftei and M. Ignat. *Ceramics International* **41** (3) 4430-4437 (2015)