

Phosphors for Improving Performance of Perovskite Solar Cells

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Abstract. In recent years, solar cells based on organic—inorganic hybrid perovskite structured materials having efficiencies comparable with that of *c - Si* solar cells have been demonstrated. In the initial experiments efficiencies were as low as 3.8 %. Since then, rapid progress has been made and the state of art perovskite based solar cells (PSC) have efficiencies as high as 17 %. However, PSC is still an emerging technology and several issues are still to be addressed before it can be commercialized. $\text{CH}_3\text{NH}_3\text{PbX}_3$, compounds absorb light in near UV as well as visible region. UV light is not converted into electrical energy. On the contrary, it degrades the cell performance over a period. A downshifting phosphor which will absorb light in 350-450 nm and emit in the green region can improve the performance of the cell. Results on synthesis and characterization of $\text{ZnB}_2\text{O}_4:\text{Mn}^{2+}$ and $\text{Ba}_9\text{Sc}_2\text{Si}_6\text{O}_{24}:\text{Eu}^{2+}$ phosphors presented here show that these can be adequate for this purpose.

INTRODUCTION

In recent years, solar cells based on organic—inorganic hybrid perovskite structured materials having efficiencies comparable with that of *c - Si* solar cells have been demonstrated. Kojima et al were first to report Organometal halide perovskites as visible-light sensitizers for photovoltaic cells [1]. Inorganic—organic perovskite compounds ($\text{CH}_3\text{NH}_3\text{PbX}_3$, X =I, Br, and Cl) have since then been considered as light harvesting materials for hybrid solar cells because of their high extinction coefficients and broader light-absorption [2-4]. Efficiencies were as low as 3.8 %. Since then, rapid progress has been made and the state of art perovskite based solar cells (PSC) have efficiencies as high as 17 % [5,6]. Coupled with these high efficiencies, other attractive features such as simple processing conditions and high absorption coefficient make PSC highly promising.

However, PSC is still an emerging technology and several issues are still to be addressed before it can be commercialized. $\text{CH}_3\text{NH}_3\text{PbX}_3$, compounds absorb light in near UV as well as visible region. Leijtens et al [7] showed a loss of charge in PSCs due to UV exposure. They proposed that the UV-degraded cells suffered from a deep trapping of injected electrons within newly available sites in the TiO_2 . This instability of PSC under UV exposure can be rectified (1) by TiO_2 surface states pacification, (2) by completely removing the mesoporous TiO_2 film, and (3) by prevention of UV light reaching to the mesoporous TiO_2 film. The third option where a suitable down-shifting (DS) material absorbs UV light (< 400 nm) falling on the PSC and re-emits visible light which is then utilized by the perovskite absorber can be an effective way of improving the efficiency while reducing the UV light induced degradation [8].

In this paper, we present results on synthesis and characterization of $\text{ZnB}_2\text{O}_4:\text{Mn}^{2+}$ and $\text{Ba}_9\text{Sc}_2\text{Si}_6\text{O}_{24}:\text{Eu}^{2+}$ phosphors. These phosphors absorb light in nUV/blue region of the spectrum and emit in the green region where the PSC solar sensitivity is high. Though these phosphors have been known for sometime, the use as a downshifting phosphor for the modification of solar spectrum is suggested for the first time.

EXPERIMENTAL

Phosphors were prepared by the conventional solid state reaction method. For preparing $\text{ZnB}_2\text{O}_4:\text{Mn}^{2+}$ phosphor, ZnO , and H_3BO_3 were thoroughly mixed in stoichiometric ratios. MnCO_3 was added for activation. The mixed powders were heated at 600 C for 2 hours followed by a second step involving heating at 850 C for 12 hours. For preparing $\text{Ba}_9\text{Sc}_2\text{Si}_6\text{O}_{24}:\text{Eu}^{2+}$ phosphors, BaCO_3 , Sc_2O_3 and SiO_2 were mixed in stoichiometric ratios. 2.5 wt.% Li_2CO_3 was added as a flux. For activation, Eu_2O_3 was used. Solid state reaction was carried out at 1100 C for 12 hours. For reducing Eu to divalent form, the phosphors were heated in the reducing atmosphere provided by burning charcoal at 950 C for 2 hours.

X-ray diffraction (XRD) patterns recorded on XPERT-PRO diffractometer using $\text{Cu K}\alpha$ ($\lambda=1.54059 \text{ \AA}$) radiation. The photoluminescence measurements were obtained using Hitachi F7200 spectrofluorimeter.

RESULTS AND DISCUSSION

Fig.1 shows xrd pattern of ZnB_2O_4 . For comparison stick pattern of ICDD 14-0002 is also shown. An excellent match is seen. A phase pure ZnB_2O_4 is thus formed. Results on PL are presented in Fig.2. An intense green

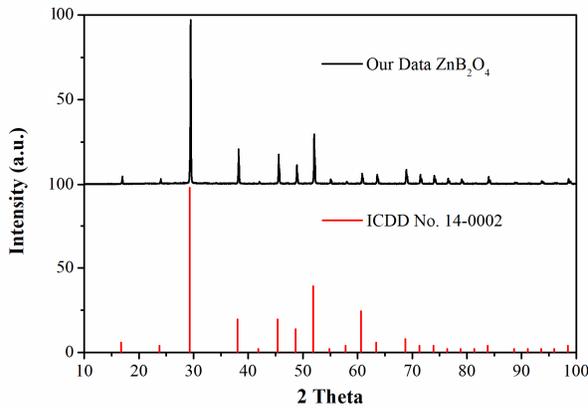


FIGURE 1 XRD pattern of ZnB_2O_4 .

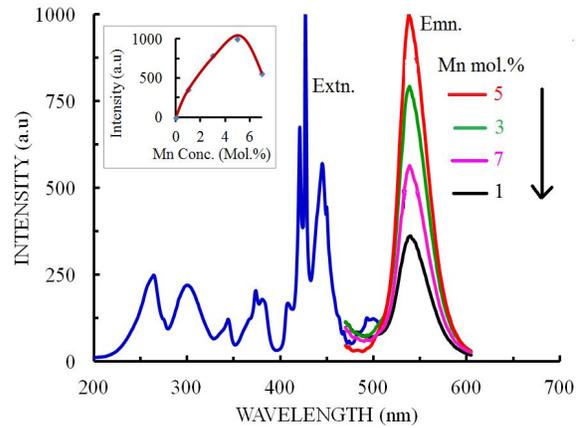


FIGURE 2 PL spectra for $\text{ZnB}_2\text{O}_4:\text{Mn}^{2+}$ phosphors.

emission with maximum around 538 nm is observed upon excitation by 450 nm. Excitation spectrum covers a wide range from 250-450 nm. Inset shows variation of the intensity of 538 nm band with Mn^{2+} concentration. Highest intensity is obtained for 5 mol.% Mn^{2+} and concentration quenching is observed for higher values. Lifetime for 538 nm emission was measured as 13.5 ms (Figure 3)

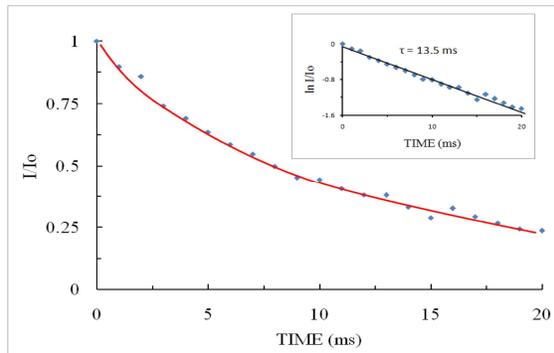


FIGURE 3 Luminescence decay of $\text{ZnB}_2\text{O}_4:\text{Mn}^{2+}$.

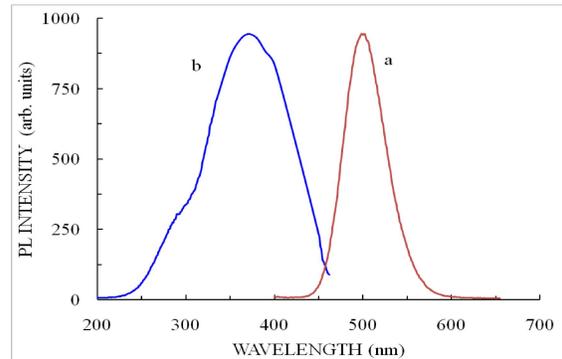


FIGURE 4 PL spectra for $\text{Ba}_9\text{Sc}_2\text{Si}_6\text{O}_{24}:\text{Eu}^{2+}$.

Results for $\text{Ba}_9\text{Sc}_2\text{Si}_6\text{O}_{24}:\text{Eu}^{2+}$ phosphor are presented in Fig.4. In previous studies, the $\text{Ba}_9\text{Sc}_2\text{Si}_6\text{O}_{24}$ based phosphors were prepared at temperatures as high as 1400 C [9,10]. Using flux, we could prepare it at 1100 C only. Again intense green emission peaking around 500 nm is observed (Fig.4, curve a). The corresponding excitation spectrum covers entire UV/violet region from about 300-430 nm.

It is thus seen that both $\text{ZnB}_2\text{O}_4:\text{Mn}^{2+}$ and $\text{Ba}_9\text{Sc}_2\text{Si}_6\text{O}_{24}:\text{Eu}^{2+}$ phosphors show emission in the green region. These can be adequate for the purpose of spectrum matching. This is further illustrated in Fig.5.

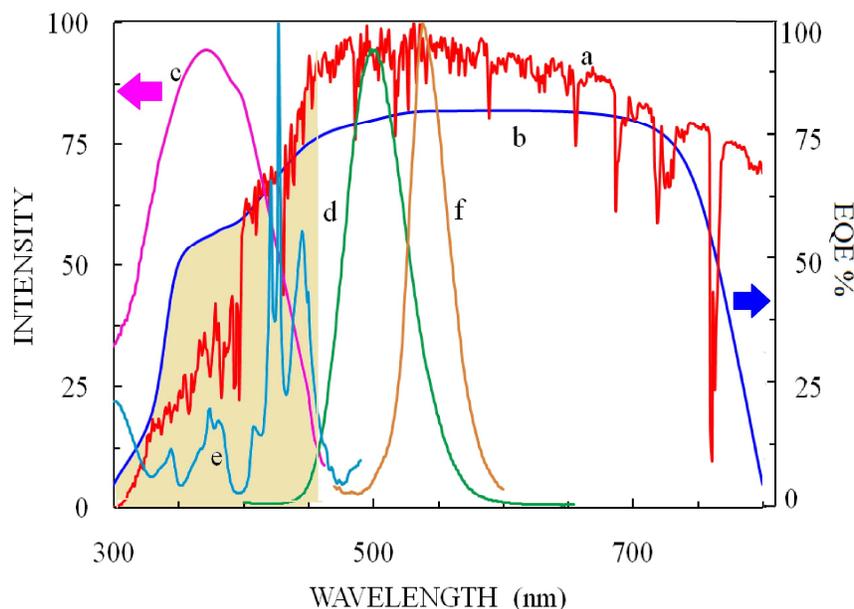


FIGURE 5. Modification of Solar Spectrum using phosphors. a> AM1.5 solar spectrum, b> spectral response of typical PSC solar cell, c> excitation and d> emission spectrum of $\text{Ba}_9\text{Sc}_2\text{Si}_6\text{O}_{24}:\text{Eu}^{2+}$. e> excitation and f> emission spectrum of $\text{ZnB}_2\text{O}_4:\text{Mn}^{2+}$. Shaded portion shows the portion of solar spectrum adequate for downshifting.

A typical spectral response of PSC [11] solar cell and emission spectrum of $\text{Ba}_9\text{Sc}_2\text{Si}_6\text{O}_{24}:\text{Eu}^{2+}$ (Fig.5, curves b and d). It can be seen that Eu^{2+} emission is located in the region where PSC shows good sensitivity. PSC external quantum efficiency (EQE) curve dips below 500 nm. On the other hand, $\text{Ba}_9\text{Sc}_2\text{Si}_6\text{O}_{24}:\text{Eu}^{2+}$ excitation curve (Fig.5, curve c) shows good overlap with the solar spectrum (Fig.5, curve a) in the region 350-450 nm. Similarly, excitation (Fig.5, curve e) and emission spectra (Fig.5, curve f) for $\text{ZnB}_2\text{O}_4:\text{Mn}^{2+}$ show good overlap with nUV/blue part of the solar spectrum and EQE curve for PSC, respectively. One may expect better utilization of solar spectrum in this region by coating PSC solar cell with thin, transparent layer of $\text{ZnB}_2\text{O}_4:\text{Mn}^{2+}$ / $\text{Ba}_9\text{Sc}_2\text{Si}_6\text{O}_{24}:\text{Eu}^{2+}$ phosphor.

CONCLUSIONS

$\text{ZnB}_2\text{O}_4:\text{Mn}^{2+}$ and $\text{Ba}_9\text{Sc}_2\text{Si}_6\text{O}_{24}:\text{Eu}^{2+}$ phosphors were prepared by solid state reaction. Both these phosphors have absorption in near UV/blue region of the spectrum and emission in the green region. These phosphors can protect PSC from UV radiations and thus decrease the degradation. Moreover, conversion of near UV/blue light to green, where PSC has high response will help improve the efficiency of PSC.

REFERENCES

1. A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, *J. Am. Chem. Soc.* **131**, 6050-6051 (2009)
2. H. S. Kim, C. R. Lee, J. H. Im, K. B. Lee, T. Moehl, A. Marchioro, S. J. Moon, R. H. Baker, J. H. Yum, J. E. Moser, M. Gratzel and N. G. Park, *Sci. Rep.* **2**, 591 (2012)
3. M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, and H. J. Snaith, *Science* **338**, 643-647 (2012)
4. L. Etgar, P. Gao, Z. Xue, Q. Peng, A. K. Chandiran, B. Liu, M. K. Nazeeruddin and M. Gratzel, *J. Am. Chem. Soc.* **134**, 17396-17399 (2012)

5. Nam-Gyu Park, *Materials Today* **18**, 65-72 (2015)
6. Qi Chen, Nicholas De Marco, Yang (Michael) Yang, Tze-Bin Song, Chun-Chao Chen, Hongxiang Zhao, Ziruo Hong, Huanping Zhou and Yang Yanga, *Nano Today* **10**, 355-396 (2015)
7. T. Leijtens, G. E. Eperon, S. Pathak, A. Abate, M. M. Lee, and H. J. Snaith, *Nat. Commun.* **4**, 2885 (2013)
8. Nikhil Chander, A. F. Khan, P. S. Chandrasekhar, Eshwar Thouti, Sanjay Kumar Swami, Viresh Dutta and Vamsi K. Komarala, *Appl. Phys. Lett.* **105**, 033904 (2014)
9. Tomoyuki Nakano, Yoshitaka Kawakami, Kazuyoshi Uematsu, Tadashi Ishigaki, Kenji Toda and Mineo Sato, *J. Lumin.* **129**, 1654–1657 (2009)
10. Liu Bian, Feifei Du, Shanshan Yang, Qingyong Ren and Q.L. Liu, *J. Lumin.* **137**, 168-172 (2013)
11. L. Qing, H. T. Chandran, H. T. Xue, M. F. Lo and C. S. Lee, *Organic Electronics* **27**, 12-17 (2015)