Conference materials
UDC 621.383.51
DOI: https://doi.org/10.18721/JPM.161.172

New inorganic materials for electron transport layers in perovskite solar cells

A.B. Nikolskaia [1]✉, S.S. Kozlov [1], O.V. Alexeeva [1],
M.F. Vildanova [1], O.K. Karyagina [1], O.V. Almjasheva [2,3],
V.V. Gusarov [2,3], O.I. Shevaleevskiy [1]

[1] Emanuel Institute of Biochemical Physics, RAS, Moscow, Russia;
[2] St. Petersburg State Electrotechnical University "LETI", St. Petersburg, Russia;
[3] Ioffe Institute, St. Petersburg, Russia
✉ anickolskaya@mail.ru

Abstract. Ternary complex oxides with cubic pyrochlore structure $Bi_xFe_yWO_q$ (BFWO) were obtained by hydrothermal synthesis at different pH values of hydrothermal fluid and were first used as electron transport layers in perovskite solar cells (PSCs). The analysis of photovoltaic parameters measured for BFWO-based PSCs demonstrated that BFWO materials obtained at pH 2 allow improving the PSC performance by ~ 4% (rel.) in comparison with state-of-the-art PSCs. In addition, BFWO-based PSCs exhibited higher tolerance to the degradation under continuous illumination.

Keywords: ternary complex oxides, electron transport layer, perovskite solar cells, solar photovoltaics

Funding: This work was supported by the Russian Science Foundation (RSF) under grant No. 20-69-47124.

Citation: Nikolskaia A.B., Kozlov S.S., Alexeeva O.V., Vildanova M.F., Karyagina O.K., Almjasheva O.V., Gusarov V.V., Shevaleevskiy O.I., New inorganic materials for electron transport layers in perovskite solar cells, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (1.1) (2023) 422–427. DOI: https://doi.org/10.18721/JPM.161.172

Материалы конференции
УДК 621.383.51
DOI: https://doi.org/10.18721/JPM.161.172

Новые неорганические материалы для электронно-транспортных слоев в перовскитных солнечных элементах

А.Б. Никольская [1]✉, С.С. Козлов [1], О.В. Алексеева [1],
М.Ф. Вильданова [1], О.К. Карягина [1], О.В. Альмяшева [2,3],
В.В. Гусаров [2,3], О.И. Шевалеевский [1]

[1] Институт биохимической физики им. Н.М. Эмануэля РАН, Москва, Россия;
[2] Санкт-Петербургский государственный электротехнический университет «ЛЭТИ» им. В.И. Ульянова (Ленина), Санкт-Петербург, Россия;
[3] Физико-технический институт им. А.Ф. Иоффе РАН, Санкт-Петербург, Россия
✉ anickolskaya@mail.ru

Аннотация. В данной работе в качестве электронно-транспортных слоев в перовскитных солнечных элементах (ПСЭ) впервые были использованы тонкие пленки тройных сложных оксидов со структурой пирохлора вида $Bi_xFe_yWO_q$ (BFWO). Анализ фотоэлектрических параметров сконструированных ПСЭ показал, что эффективность образца со слоем BFWO на 4% выше, чем у ПСЭ на основе стандартно используемого слоя TiO_2. Кроме того, ПСЭ с материалом BFWO демонстрировали повышенную устойчивость к непрерывному освещению.

Ключевые слова: тройные сложные оксиды, электронно-транспортный слой, перовскитные солнечные элементы, солнечная фотовольтаика

Финансирование: Исследование выполнено за счет гранта Российского научного фонда (проект № 20-69-47124).

Ссылка при цитировании: Никольская А.Б., Козлов С.С., Алексеева О.В., Вильданова М.Ф., Карягина О.К., Альмяшева О.В., Гусаров В.В., Шевалеевский О.И. Новые неорганические материалы для электронно-транспортных слоев в перовскитных солнечных элементах // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 1.1. С. 422–427. DOI: https://doi.org/10.18721/JPM.161.172

Introduction

In the last decade, perovskite solar cells (PSCs) based on hybrid materials with perovskite-like structure with the general formula ABX_3 (A — $CH_3NH_3^+$, $HC(NH_2)^{2+}$, B — Pb^{2+}, Sn^{2+}, X — I^-, Br^- or Cl^-) became a major alternative to conventional crystalline silicon solar cells [1, 2, 3]. In hybrid perovskite materials organic and inorganic components alternate with each other. Due to this perovskite compounds used in PSCs exhibit unique electrical and optical properties, while the power conversion efficiency (PCE) for PSCs exceeds 25% [4, 5]. The photovoltaic characteristics (PV) and long-term stability of PSCs are significantly affected by the electron transport layer (ETL) on the surface of which perovskite material is deposited [6, 7].

The semiconductor material for the ETL layer must show high transmittance characteristics and provide good band alignment with contact. At the same time, ETL should effectively block photogenerated holes to reduce the recombination processes at the perovskite/ETL interface [8, 9]. Generally mesoscopic layer based on titanium dioxide (TiO_2) with a band gap of E_g = 3.2 eV is used as ETL [6]. TiO_2-based PSCs demonstrate high PCE, but degrade significantly over time [10]. The degradation processes in PSCs are partially explained by the instability of the TiO_2 material under UV radiation where the continuous illumination causes desorption of oxygen molecules from TiO_2 layer thus initiating degradation of the perovskite layer [10, 11]. In this regard, the search of new materials with increased resistance to the UV radiation for ETLs in PSCs is an important issue for perovskite photovoltaics. For this purpose, ternary complex oxides are of great interest [12]. These materials are characterized by high electron mobility, high density of chemical sites, tunable band structures and high chemical stability even under extreme conditions [6, 13].

In this work, complex oxides formed in the ternary system Bi_2O_3–Fe_2O_3–WO_3 were obtained by hydrothermal synthesis at different pH values of hydrothermal fluid. The synthesized $Bi_xFe_yWO_q$ powders (BFWO) were examined by X-ray and optical methods and used to fabricate ETLs for PSCs. PV properties of the PSCs based on BFWO layers were investigated under standard illumination conditions (AM1.5G, 1000 W/m^2). The comparative analysis of the results obtained revealed a new approach to develop efficient PV devices with high tolerance to the degradation under continuous illumination.

Materials and Methods

The BFWO powders were obtained by hydrothermal synthesis at hydrothermal fluid pH values of 2, 5 and 7 according to procedure described in [14] and were mixed with acetic acid, terpineol, ethyl cellulose and ethanol to obtain thick pastes as specified in [15]. These pastes were diluted in ethanol (1:5), sonicated in ultrasonic bath several times and were deposited by spin coating (3000 rpm, 30 s) onto FTO (fluorine doped SnO_2) conductive glass substrates (Solaronix, 2×2 cm) with subsequent annealing at 500 °C for 1 hr [16]. Thus, the mesoporous ETL thin films based on BFWO were obtained. State-of-the-art TiO_2-based ETL thin film was fabricated using the same technique for comparative analysis.

PSCs were fabricated under ambient conditions at relatively high humidity (~ 50–60%) according to the procedure described in detail earlier [17]. Perovskite ($CH_3NH_3PbI_3$) layer was formed on ETL surface using a conventional one-step deposition method [18]. A layer of Spiro-MeOTAD hole transport material was spin-coated onto the surface of the perovskite layers. The final stage of PSC fabrication was the deposition of ~ 50-nm thick Au contacts by vacuum thermal evaporation using the VUP-4 vacuum post.

The X-ray diffraction (XRD) study of BFWO powders was performed by a DRON-3M X-ray diffractometer with Cu Kα radiation (λ = 1.5405 Å) as the X-ray source. The optoelectronic properties of BFWO powders were characterized using UV-vis spectroscopy (Shimadzu UV-3600 spectrophotometer with an ISR-3100 integrating sphere in the wavelength range of 300–1200 nm). The PV measurements for PSCs fabricated were provided under standard illumination conditions of 1000 W/m^2 (AM1.5G) using Abet 10500 solar simulator (Abet Technologies, USA). The current density–voltage (*J–V*) characteristics were measured by Semiconductor Characterization System 4200-SCS (Keithley, USA). PSCs were masked to obtain working area of 0.08 cm^2.

Results and Discussion

The chemical composition of BFWO powders obtained by hydrothermal synthesis at different pH values of hydrothermal fluid was determined by energy dispersive X-ray microanalysis (EDXMA) and is listed in Table 1 (more detailed information in [14]). The samples obtained at pH 2 and 5 have a similar composition. With an increase in pH from 5 to 7, the samples become more enriched with W and Fe ions. According to [14] BFWO particles with the average size of 30–35 nm tend to form spherical aggregates of crystallites. The room temperature XRD patterns of BFWO powders are shown in Fig. 1. The peaks indicate that all samples are single-phase, and their crystal structure corresponds to that of cubic pyrochlore. The samples contain no impurities. Obtained data are in good agreement with literature data.

The optical band gaps E_g of the BFWO powders obtained were calculated from the diffusion reflectance UV-vis spectra after Kubelka-Munk conversion and Tauc plot treatment for indirect transition (Fig. 2, *a*) [19]. It was found to be 2.60 eV for pH = 2, 2.35 eV for pH = 5 and 2.48 for pH = 7. These results indicate that the BFWO materials have the properties of semiconductors and can be used for PSCs development. It is also shown that the optoelectronic characteristics of BFWO samples are significantly influenced by hydrothermal synthesis conditions, especially pH value of hydrothermal fluid.

Table 1

The composition of BFWO powders [14]

pH	Formula
2	$Bi_{0.50}Fe_{0.34}WO_q$
5	$Bi_{0.51}Fe_{0.36}WO_q$
7	$Bi_{0.70}Fe_{0.45}WO_q$

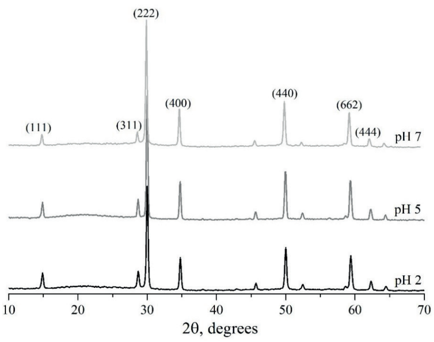

Fig. 1. XRD patterns of BFWO samples obtained at different pH values of hydrothermal fluid

The BFWO ETLs were fabricated on the surface of FTO conductive glasses by spin coating of thick pastes made by mixing BFWO powders with organic binders. PSCs with the cell architecture of FTO/BFWO/$CH_3NH_3PbI_3$/Spiro-OMeTAD/Au were fabricated using these ETLs under ambient conditions. State-of-the-art PSC based on TiO_2 mesoporous layer was also constructed for comparison.

J-V curves recorded under standard illumination (1000 W/m^2, AM1.5G) for PSCs with BFWO ETLs

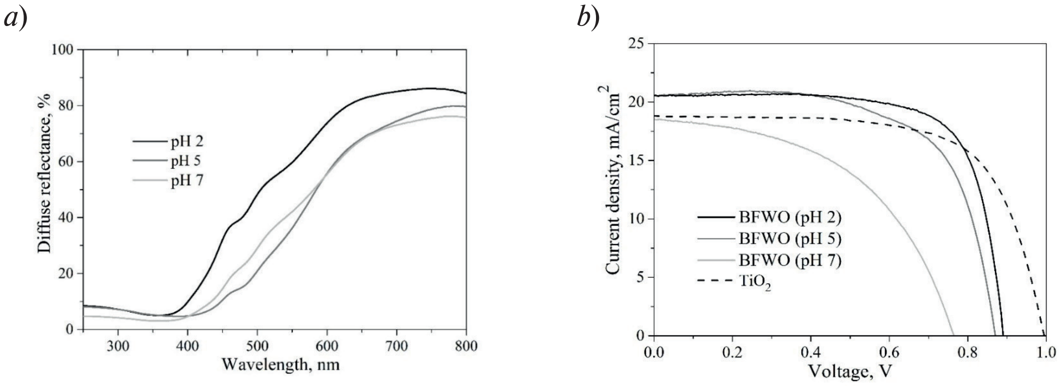

Fig. 2. Reflectance spectra of the BFWO samples at different pH values of hydrothermal fluid (*a*), *J*–*V* curves for the PSC devices based on different ETLs (*b*)

Table 1

The PV characteristics of PSC devices based on different ETLs

ETL	J_{SC}, mA/cm^2	V_{OC}, V	FF, a.u.	PCE, %
TiO_2	18.8 ± 0.18	1.00 ± 0.02	0.69 ± 0.02	12.8 ± 0.17
BFWO pH=2	20.5 ± 0.17	0.89 ± 0.01	0.73 ± 0.01	13.3 ± 0.15
BFWO pH=5	20.5 ± 0.21	0.87 ± 0.02	0.66 ± 0.02	11.8 ± 0.23
BFWO pH=7	18.5 ± 0.17	0.77 ± 0.02	0.49 ± 0.03	7.0 ± 0.17

obtained at different pH values of hydrothermal fluid and with TiO_2 ETL are shown in Fig. 2, *b*. The PV parameters for all PSCs including short circuit current density (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF) and power conversion efficiency (PCE) are listed in Table 2. It can be seen that the PSCs based on the BFWO compounds obtained at pH = 2 ($Bi_{0.50}Fe_{0.34}WO_q$) and 5 ($Bi_{0.51}Fe_{0.36}WOq$) showed PCE values of 13.3% and 11.8%, respectively, which is comparable to the efficiency obtained for state-of-the-art PSCs (Table 2). PSC based on the BFWO compound obtained at pH = 7 ($Bi_{0.7}0Fe_{0.45}WO_q$) showed poor PV performance, which was manifested in the decreased V_{OC} and FF values. The highest PCE is demonstrated in the PSC samples with BFWO-based ETLs obtained at hydrothermal fluid pH 2 and it is ~ 4% (rel.) higher than for TiO_2-based device. The data obtained confirms that BFWO materials can be used as a prospective ETL alternative in the efficient and stable PSCs.

It should be noted that for the BFWO-based PSCs the PV characteristics were obtained for the voltage sweep during *J*-*V* curve measurements started from 3 V. Previously, similar effects were observed for solar cells based on ferroelectric transition-metal oxides and were explained by the electromigration of charged defects (oxygen vacancies) and switching the ferroelectric polarization [20]. Also in contrast to state-of-the-art PSCs with TiO_2 ETL there is no compact layer in BFWO-based samples what indicates good blocking properties of BFWO thin films.

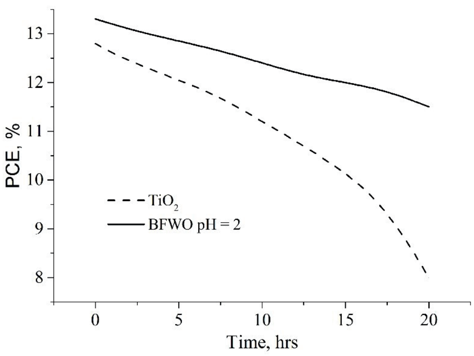

Fig. 3. Stability test of the PSCs under continuous illumination (AM1.5, 1000 W/m^2)

PV parameters of PSCs with BFWO and TiO_2 ETLs were investigated under continuous standard illumination conditions (AM1.5, 1000 W/m^2) and under ambient conditions. The appropriate results are presented in Fig. 3. The data obtained revealed that BFWO-based samples demonstrate more stable behavior than TiO_2-based devices.

We have shown that ternary complex oxides such as $Bi_xFe_yWO_q$ with cubic pyrochlore structure demonstrate semiconductor properties and can be successfully used as ETL materials for the fabrication of high efficient and stable PSCs. These new inorganic materials have shown the better resistance to the degradation under continuous UV radiation than state-of-the-art ETLs. More of it their optical and photoelectrical properties can be easily tuned by synthetic conditions, especially by changing pH value of hydrothermal fluid.

Conclusion

In this paper complex oxide phases formed in the ternary system Bi_2O_3–Fe_2O_3–WO_3 were obtained by hydrothermal synthesis at different pH values of hydrothermal fluid and were used to fabricate the ETLs for PSCs. The $Bi_xFe_yWO_q$ powders (BFWO) were examined by X-ray and optical methods. Energy bandgaps values were calculated and were found to be 2.3–2.6 eV depending on pH value of hydrothermal fluid. PSCs with the cell architecture of FTO/BFWO/$CH_3NH_3PbI_3$/Spiro-OMeTAD/Au were fabricated under ambient conditions. The highest PCE value was demonstrated by the PSC samples with BFWO ETL obtained at hydrothermal fluid pH 2 and it was ~ 4% (rel.) higher than for TiO_2-based device. We have shown that BFWO-based PSCs possessed higher tolerance to the degradation under continuous illumination conditions (AM1.5G, 1000 W\m^2) in comparison with conventional PSCs. The obtained results revealed a new approach to develop efficient PV devices with the increased resistance to UV radiation.

REFERENCES

1. **Wang R., Mujahid M., Duan Y., Wang Z.K., Xue J., Yang Y.,** A review of perovskites solar cell stability, Adv. Funct. Mater. 29 (47) (2019) 1808843.

2. **Tejeda A., Choy W.C.H., Deleporte E., Graetzel M.,** Special issue on hybrid perovskites for photovoltaics and optoelectronics, J. Phys. D: Appl. Phys. 53 (7) (2020) 070201.

3. **Green M.,** Photovoltaic technology and visions for the future, Prog. Energ. 1 (1) (2019) 013001.

4. **Park N.G.,** Research direction toward scalable, stable, and high efficiency perovskite solar cells, Adv. Energ. Mater. 10 (13) (2020) 1903106.

5. **Green M.A., Dunlop E.D., Hohl-Ebinger J., Yoshita M., Kopidakis N., Hao X.,** Solar cell efficiency tables (version 57), Prog. Photovolt.: Res. Appl. 29 (1) (2021) 3–15.

6. **Wang K., Olthof S., Subhani W.S., Jiang X., Cao Y., Duan L., Wang H., Du M., Liu S.,** Novel inorganic electron transport layers for planar perovskite solar cells: progress and prospective, Nano Energy. 68 (2020) 104289.

7. **Mahmood K., Sarwar S., Mehran M.T.,** Current status of electron transport layers in perovskite solar cells: materials and properties, RSC Adv. 7 (28) (2017) 17044–17062.

8. **Noh M. F. M., Teh C.H., Daik R., Lim E.L., Yap C.C., Ibrahim M.A., Ludin N.A., Yusoff A.R., Jang J., Teridi M.A.M.,** The architecture of the electron transport layer for a perovskite solar cell, J. Mater. Chem. C. 6 (4) (2018) 682–712.

9. **Yang G., Tao H., Qin P., Kea W., Fang G.,** Recent progress in electron transport layers for efficient perovskite solar cells, J. Mater. Chem. A. 4 (11) (2016) 3970–3990.

10. **Leijtens T., Eperon G.E., Pathak S., Abate A., Lee M.M., Snaith H.,** Overcoming ultraviolet light instability of sensitized TiO2 with meso-superstructured organometal tri-halide perovskite solar cells, Nat. Comm. 4 (1) (2013) 1–8.

11. **Yuan Y., Ji Z., Yan G., Li Z., Li J., Kuang M., Jiang B., Zeng L., Pan L., Mai W.,** TiO_2 electron transport bilayer for all-inorganic perovskite photodetectors with remarkably improved UV stability toward imaging applications, J. Mater. Sci. Tech. 75 (2021) 39–47.

12. **Zhou Y., Li X., Lin H.,** To be higher and stronger–metal oxide electron transport materials for perovskite solar cells, Small. 16 (15) (2020) 1902579.

13. **Thambidurai M., Shini F., Harikesh P.C., Mathews N., Dang C.,** Highly stable and efficient planar perovskite solar cells using ternary metal oxide electron transport layers, J. Power Sourc. 448 (2020) 227362.

14. **Proskurina O.V., Sergeev A.A., Buryanenko I.V., Semenov V.G., Voznesenskiy S.S., Gusarov V.V.,** Crystal structure and optical properties of the Bi-Fe-W-O pyrochlore phase synthesized via a hydrothermal method, J. Alloy. Comp. 889 (2022) 161598.

15. **Ito S., Chen P., Comte P., Nazeeruddin M.K., Liska P., Pechy P., Gratzel M.,** Fabrication of screen-printing pastes from TiO2 powders for dye-sensitised solar cells, Prog. Photovolt: Res. Appl. 15 (7) (2007) 603–612.

16. **Nikolskaia A., Vildanova M., Kozlov S., Tsvetkov N., Larina L., Shevaleevskiy O.,** Charge transfer in mixed-phase TiO_2 photoelectrodes for perovskite solar cells, Sustainability. 12 (3) (2020) 788.

17. **Vildanova M.F., Nikolskaia A.B., Kozlov S.S., Shevaleevskiy O.I., Almjasheva O.V., Gusarov V.V.,** Group IV oxides for perovskite solar cells, Dokl. Phys. Chem. 496 (2) 2021 13–19.

18. **Kozlov S.S., Larina L.L., Nikolskaia A.B., Almjasheva O.V., Proskurina O.V., Shevaleevskiy O.I.,** Solar cells based on complex oxides, Tech. Phys. Lett. 47 (4) (2021) 283–286.

19. **Tauc J., Grigorovici R., Vancu A.,** Optical properties and electronic structure of amorphous germanium, Phys. Status Solidi. 15 (2) (1966) 627–637.

20. **Wang L., Ma C., Wu T., Ma H., Yuan G., Chang L., Wang J.,** Ferroelectric $BiFeO_3$ as an oxide dye in highly tunable mesoporous all-oxide photovoltaic heterojunctions, Small. 13 (1) (2017) 1602355.

THE AUTHORS

NIKOLSKAIA Anna B.
anickolskaya@mail.ru
ORCID: 0000-0002-7430-4133

KOZLOV Sergey S.
sergeykozlov1@gmail.com
ORCID: 0000-0002-8660-5646

ALEXEEVA Olga V.
alexol@yandex.ru
ORCID: 0000-0001-8982-3959

VILDANOVA Marina F.
mvildanova@sky.chph.ras.ru
ORCID: 0000-0002-5720-6048

KARYAGINA Olga K.
olgakar07@mail.ru
ORCID: 0000-0002-6702-5195

ALMJASHEVA Oksana V.
almjasheva@mail.ru
ORCID: 0000-0002-6132-4178

GUSAROV Victor V.
victor.v.gusarov@gmail.com
ORCID: 0000-0003-4375-6388

SHEVALEEVSKIY Oleg I.
shevale2006@yahoo.com
ORCID: 0000-0002-8593-3023

Received 28.10.2022. Approved after reviewing 08.11.2022. Accepted 08.11.2022.