

Synthesis and properties of electrodes based on BiFeO₃/La₂NiMnO₆ composite thin films for photoelectrochemical water splitting

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The paper reveals synthesis and investigation of thin films based on composite materials BiFeO₃/La₂NiMnO₆ where BiFeO₃ is a multiferroic compound and La₂NiMnO₆ is a double perovskite. Using these materials photoanodes for „green“ hydrogen production by photoelectrochemical water splitting were fabricated. The BiFeO₃/La₂NiMnO₆ composites with La₂NiMnO₆ content of 50 mass% demonstrated the improved photocatalytic properties in comparison with BiFeO₃ material and its use as photoanode allowed to increase the efficiency of hydrogen production by water electrolysis.

Keywords: green hydrogen, water electrolysis, electrodes, composite materials.

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The key objective of modern global power engineering is the transition to resource-saving technologies and large-scale implementation of renewable energy sources [1]. „Green“ hydrogen, which is generated in the process of electrolysis of water under the influence of solar radiation energy [2], is considered to be one of the most promising and environmentally friendly energy sources. The development of highly efficient electrolytic water splitting systems and the search for new high-conductivity electrode materials resistant to an aqueous environment are important tasks in this context [3]. Multiferroics, which are characterized both by a high carrier transport rate and by a high efficiency of carrier separation under the influence of an external electric field, have the parameters needed for this purpose [4]. The chemically stable BiFeO₃ (BFO) compound with a perovskite structure is particularly noteworthy, since it is easy to synthesize it from inexpensive materials [5]. However, the photocatalytic properties of this material put a limit on the efficiency of generation of „green“ hydrogen in the process of water electrolysis [5,6]. One way to solve this problem is to create new types of BFO-based composite materials with improved photovoltaic and catalytic properties [6].

In the present study, thin films of composite materials of the BFO/LNMO type, where LNMO is a compound with the La₂NiMnO₆ structure that belongs to the class of double perovskites and is characterized by high photosensitivity, are synthesized and examined. LNMO was also chosen for its significantly narrower band gap (~1 eV), longer carrier lifetime, and higher stability.

Thin films of BFO, LNMO, and BFO/LNMO with different LNMO concentrations (20, 50, and 80 mass%)

were synthesized by the „soft chemistry“ method. The corresponding precursors (Bi(NO₃)₃ · 5H₂O, Fe(NO₃)₃ · 9H₂O, La(NO₃)₃ · 6H₂O, Ni(NO₃)₂ · 6H₂O, and Mn(NO₃)₂ · 6H₂O) in stoichiometric quantities were dissolved in a mixture of 2-ethoxyethanol and acetic acid (volume ratio 4:1). The obtained solutions were applied to the substrate surface by spin-coating at 3000 rpm for 30 s, which was followed by annealing for 3 h in a muffle furnace at 600 °C. The thickness of the obtained layers was 300–400 nm.

Non-conducting (float) glass was used as a substrate to study the structural, morphological, and optical properties of BFO, LNMO, and BFO/LNMO thin films. To form electrodes and examine the photocatalytic properties, the studied films were applied to glass substrates coated with a conductive layer of FTO (tin oxide SnO₂ doped with F⁻ fluorine ions) and a thin layer of TiO₂ nanoparticles.

X-ray diffraction analysis (XRD) was performed using a DRON-3M (Russia) diffractometer. Optical data were obtained using a Shimadzu UV-3600 spectrophotometer with an ISR-3100 integrating sphere (Japan). The surface morphology of samples was studied by atomic force microscopy (AFM) with an NTEGRA Prima (NT-MDT, Russia) microscope. The efficiency of water electrolysis under the influence of light was measured using the designed electrodes by linear-sweep voltammetry in an electrochemical cell with a platinum counter electrode. The electrolyte was 1 M KOH. Current–voltage curves were recorded using a 4200-SCS measuring system (Keithley, United States) with an Abet 10500 solar radiation simulator (Abet Technologies, United States) under standard AM1.5G illumination conditions (1000 W/m²).

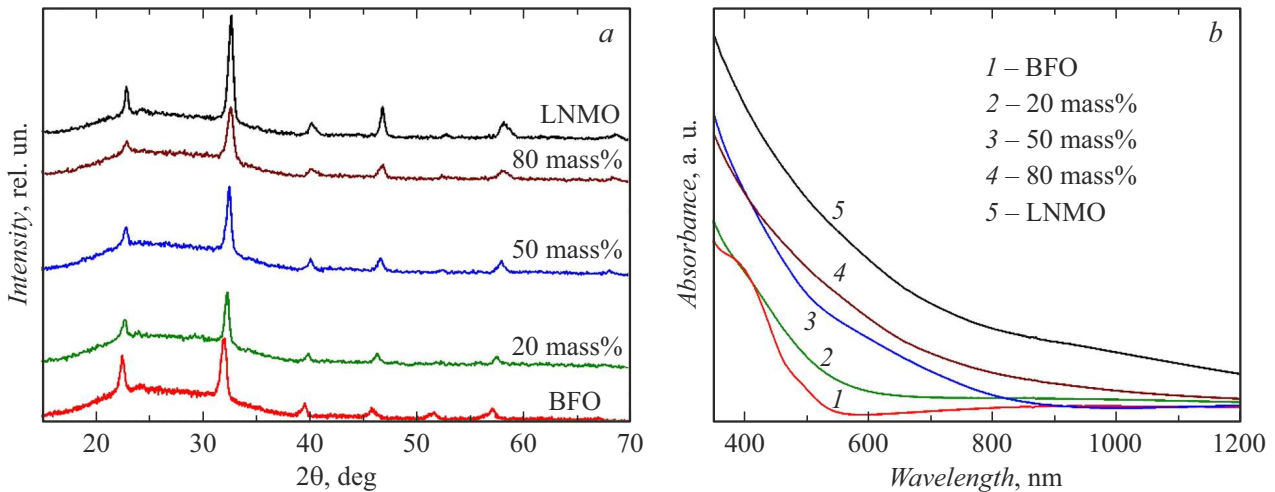


Figure 1. Diffraction patterns (a) and optical absorption spectra (b) of BFO, LNMO, and BFO/LNMO thin films with different LNMO concentrations (20, 50, and 80 mass%).

The phase composition of the synthesized BFO, LNMO, and BFO/LNMO thin films with different LNMO concentrations (20, 50, and 80 mass%) was confirmed by XRD data. The corresponding diffraction patterns are shown in Fig. 1, a; the positions of identified peaks correlate well with literature data [7]. BFO and LNMO crystalline phases are assumed to coexist in the bulk of composite BFO/LNMO films.

Figure 1, b shows the absorption spectra for BFO, LNMO, and BFO/LNMO thin films synthesized on non-conducting glass substrates. The values of band gap E_g (Table 1) were calculated based on these data using the Tauc formula for direct transitions [8]. It can be seen that the BFO thin film absorbs light within a narrow range of the visible spectrum, which limits the applicability of this material in photocatalysis. However, with an increase in LNMO phase content in the BFO/LNMO composite sample, the E_g value drops down to 1.5 eV, increasing significantly the fraction of light absorbed within the visible range. The obtained data illustrate the possibility of optimizing the optical characteristics of BFO/LNMO composite films by altering their composition, which opens up prospects for the development of new materials with improved photocatalytic properties.

The morphological characteristics of BFO, LNMO, and BFO/LNMO thin films on non-conducting glass substrates were studied by AFM. Figure 2 shows AFM images of

Table 1. Band gap E_g (in eV) for BFO, LNMO, and BFO/LNMO thin films

BFO	BFO/LNMO			LNMO
	20 mass%	50 mass%	80 mass%	
2.8	2.4	1.7	1.5	1.1

the surface of all examined samples. It is evident that all films were continuous, and the particle diameter in them varied within the range of 10–70 nm. As the LNMO content increased to 50 mass%, the surface of composite films grew more uniform: the particle size and the number of gaps between them decreased. However, the BFO/LNMO sample with an LNMO concentration of 80 mass% became non-uniform, which was confirmed by calculations based on AFM data with the values of root-mean-square surface roughness S_q and mean particle size d taken into account (Table 2). As the LNMO content in the samples increased, the above parameters first decreased significantly (by a factor of 7–8), reaching their minimum in the BFO/LNMO (50 mass%) sample, and then increased again.

Summarizing the above data, one may conclude that the inclusion of LNMO in a BFO layer and variation of their ratio provide an opportunity to adjust the optical and structural properties of samples based on them. It should also be noted that the method for synthesizing thin films of BFO/LNMO composite materials proposed here makes it possible to obtain high-quality thin nanolayers with a minimum particle size (down to 16 nm). This method turned out to be more efficient and less labor-intensive than the sol-gel method that is frequently discussed in literature [7].

Figure 3 presents the current-voltage characteristics of water electrolysis under the influence of light recorded using the fabricated photoanodes. The highest electrolysis efficiency was observed in experiments with electrodes based on BFO/LNMO (50 mass%) thin films. This may be attributed to the fact that the BFO/LNMO film with this composition had the optimum optoelectronic and morphological properties.

The studies revealed that the synthesized BFO/LNMO composite materials and photoanodes based on them are

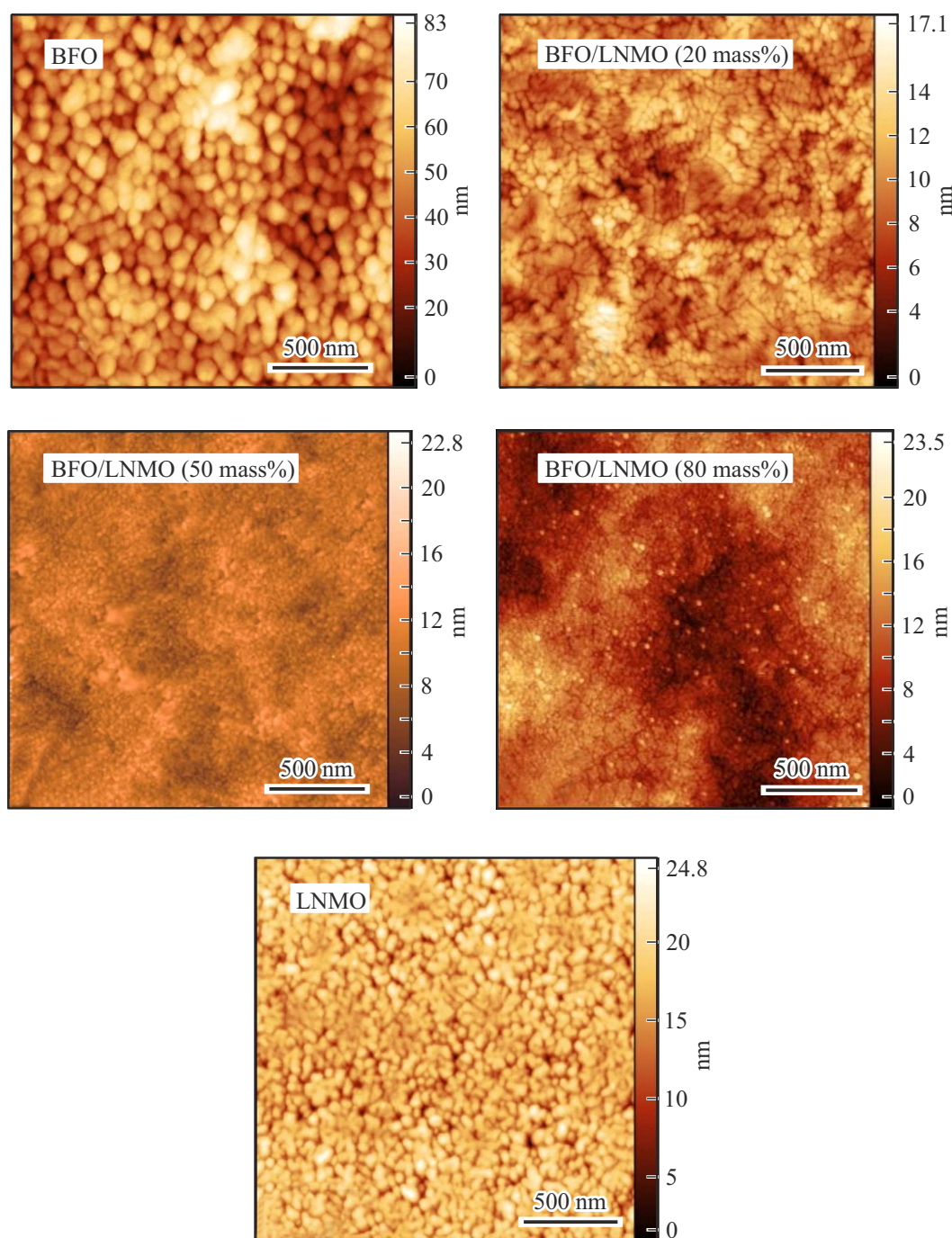


Figure 2. AFM images of the surface of BFO, LNMO, and BFO/LNMO thin films.

well suited for application in electrolytic systems for generation of „green“ hydrogen. It was demonstrated that the synthesized BFO/LNMO composites have better structural properties and a narrower band gap than the BFO compound, providing a significant potential increase in the yield of hydrogen during electrolysis. The best results were obtained in experiments with a photoanode based on a BFO/LNMO composite material where the constituent compounds were mixed in equal proportion by mass (1:1).

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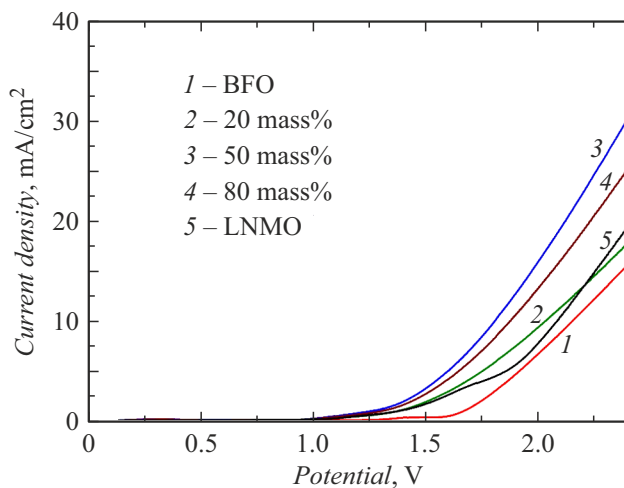
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Conflict of interest

The authors declare that they have no conflict of interest.

Table 2. Root-mean-square surface roughness S_q and mean particle diameter d for BFO, LNMO, and BFO/LNMO thin films

Concentration of LNMO, mass%	S_q , nm	d , nm
0	11.6 ± 0.9	130 ± 1
20	2.3 ± 0.7	67 ± 1
50	1.7 ± 0.4	16.7 ± 0.3
80	3.0 ± 0.9	37.9 ± 0.5
100	2.1 ± 0.1	87 ± 2

**Figure 3.** Current-voltage curves for photoanodes based on BFO, LNMO, and BFO/LNMO thin films with different LNMO content (20, 50, and 80 mass%) recorded in the process of water electrolysis in a 1 M KOH solution.

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