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A.A. Glinskaya, PhD (Chemistry), senior lecturer (BSTU, Minsk),
G.S. Petrov, PhD (Chemistry), assistant professor (BSTU, Minsk);
V.I. Romanovski, PhD, senior researcher (IGIC NAS of Belarus)

CRYSTAL STRUCTURE, MAGNETIC AND PHOTOCATALYTIC PROPERTIES OF SOLID SOLUTIONS

$\text{Bi}_{2-x}\text{La}_x\text{Fe}_4\text{O}_9$ ($x = 0; 0,05; 0,1$)

The $\text{Bi}_2\text{Fe}_4\text{O}_9$ bismuth ferrite is an important functional material that can be used as a semiconductor gas sensor and a catalyst for ammonia oxidation to NO in the commercial-scale production of nitric acid, capable of replacing expensive and deficient catalysts [1–2]. In recent years, evidence has emerged that $\text{Bi}_2\text{Fe}_4\text{O}_9$ possesses multiferroic properties; that is, the magnetic properties of this material can be controlled by an electric field and, vice versa, its electrical polarization can be modulated by a magnetic field. This suggests that $\text{Bi}_2\text{Fe}_4\text{O}_9$ and related solid solutions are potentially attractive materials for creating fundamentally new devices in the field of information and energy-saving technologies, magnetic memory and spintronic devices, magnetic field sensors, etc.

The bulk samples were prepared by ceramic method from corresponding oxides of high purity. The photocatalytic activity of the $\text{Bi}_{1,9}\text{La}_{0,1}\text{Fe}_4\text{O}_9$ powder was studied by the degradation of the Acid Telon Blue dye (ATB) in an aqueous solution, under continuous stirring and exposure in the ultraviolet (UV) radiation. 100 ml of aqueous solution (in deionized water) was prepared by completely dissolving 1,0 mg of ATB dye and then dispersing 0,010; 0,020; 0,030 or 0,040 g/l of $\text{Bi}_{1,9}\text{La}_{0,1}\text{Fe}_4\text{O}_9$ powder. The resulting suspension was equilibrated by stirring in the dark for 1 h to stabilize the adsorption of the ATB dye over the surface of the $\text{Bi}_{1,9}\text{La}_{0,1}\text{Fe}_4\text{O}_9$ powders. The stable aqueous suspensions under the continuous magnetic stirring were irradiated with the UV light using the DRT-240 lamp (with radiant stream 24,6 W) as the UV source, which emitted the UV radiation with the wavelength within the range of 240–320 nm. Following the UV radiation exposure, 5 ml of aqueous suspension was taken out of the UV chamber for each 15 min time interval for a total of 90 min of UV radiation exposure for obtaining the dye degradation efficiency.

The results of X-ray diffraction analysis made it possible to establish that the substitution of up to 10 mol.% of Bi^{3+} ions by La^{3+} ions in $\text{Bi}_2\text{Fe}_4\text{O}_9$ ferrite led to the formation of a continuous series of solid solutions. This is evidenced by a gradual decrease in parameter a and an increase in the angle α of the crystal lattice of rhombohedrally distorted perovskite. It should be noted that the studied samples contained an insignificant amount of impurity phase of ferrite BiFeO_3 (fig. 1).

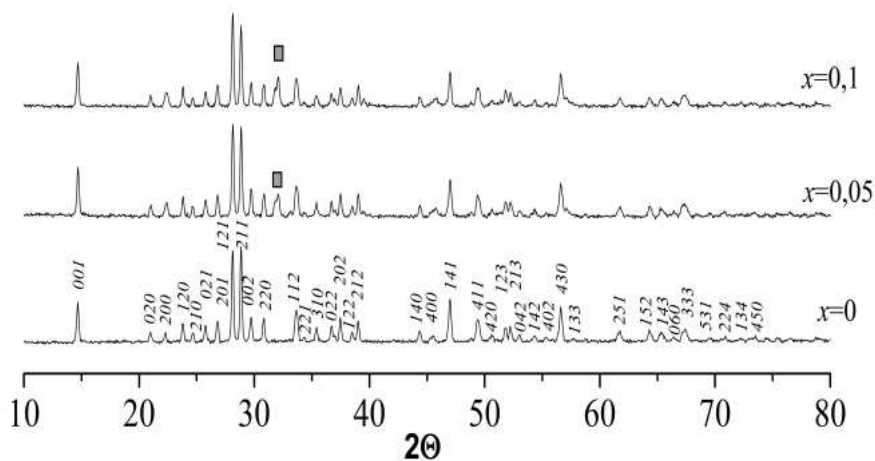


Figure 1 – XRD pattern diffracted of samples $\text{Bi}_{2-x}\text{La}_x\text{Fe}_4\text{O}_9$ at different values of x : 0 (1); 0,05 (2); 0,1 (3)

The temperature of the maximum in specific magnetization curves, obtained in the ranges 5–300 and 77–950 K, is 258 K, which corresponds to the Neel temperature, at which $\text{Bi}_2\text{Fe}_4\text{O}_9$ undergoes an antiferromagnetic-to-paramagnetic phase transition. In addition, the specific magnetization (σ_s) of the solid solutions gradually increases with increasing x (fig. 2). The increase in specific magnetization upon substitution of La^{3+} , which have a smaller ionic radius than bismuth ions, for Bi^{3+} in $\text{Bi}_2\text{Fe}_4\text{O}_9$ is probably due to distortion of the crystal structure of the solid solutions and changes in $\text{Fe}^{3+} - \text{O}^{2-} - \text{Fe}^{3+}$ indirect exchange interactions.

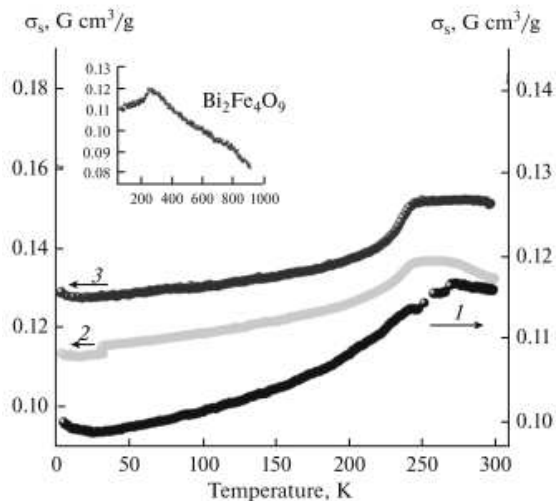


Figure 2 – Temperature dependences of specific magnetization (σ_s) for the $\text{Bi}_{2-x}\text{La}_x\text{Fe}_4\text{O}_9$ samples in 5–300 K: $x =$ (1) 0; (2) 0,05; (3) 0,1

We described the kinetics of the ATB decomposition reaction by the formal pseudo-first-order model as expressed in literature [3]: $\ln(C_0/C) = k \cdot t$, where t – irradiation time, k – reaction rate constant, C_0 – initial concentration, and C – current concentration of the ATB dye for the

t . The plots of $\ln(C_0/C)$ versus t are approximately straight lines for the various doses showing the apparent first-order rate constants (fig. 3b).

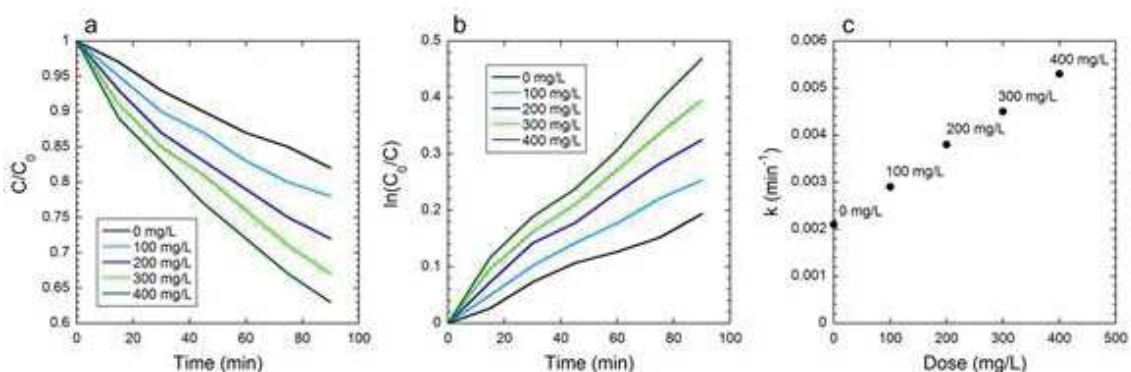


Figure 3 – Residual ATB dye concentration as a function of UV radiation exposure time (a), typical plots for determining the k (b) and the k (c) obtained for the different content of $\text{Bi}_{1,9}\text{La}_{0,1}\text{Fe}_4\text{O}_9$

The k increases with increasing content of $\text{Bi}_{1,9}\text{La}_{0,1}\text{Fe}_4\text{O}_9$. The reaction rate constant k were 0,0053; 0,0045; 0,0038 and 0,0029 min^{-1} for the 400, 300, 200 and 100 mg/l respectively (fig. 5c). The reaction rate constant k without $\text{Bi}_{1,9}\text{La}_{0,1}\text{Fe}_4\text{O}_9$ was 0,0021 min^{-1} .

Thus, the ATB solution without $\text{Bi}_{1,9}\text{La}_{0,1}\text{Fe}_4\text{O}_9$ show small changes under UV-light irradiation (up to 17,6 % efficiency after 90 min). The presence of 100–400 mg/l of $\text{Bi}_{1,9}\text{La}_{0,1}\text{Fe}_4\text{O}_9$ shows the best activity (about 37,4 %).

LITERATURE

1. Ruan Q.-J. Tunable Morphology of $\text{Bi}_2\text{Fe}_4\text{O}_9$ Crystals for Photocatalytic Oxidation / Q.-J. Ruan, W.-D. Zhang / J. Phys. Chem. – 2009. – Vol. 113. – P. 4168–4173.
2. Size-Dependent Magnetic, Photoabsorbing, and Photocatalytic Properties of Single-Crystalline $\text{Bi}_2\text{Fe}_4\text{O}_9$ Semiconductor Nanocrystals / Q. Zhang [et al.] / J. Phys. Chem. C. – 2011. – Vol. 115. – P. 25241–25246.
3. Photocatalytic Activity of Sol–Gel-Derived Nanocrystalline Titania / Baiju K. V., Shukla S., Sandhya K. S. et al. / J. Phys. Chem. C. –2007. – Vol. 111. – P. 7612–7622.