The aim of the work is the synthesis of nanostructures based on lanthanum fluoride, promising for use in photodynamic therapy of tumors in organs of cranial cavity and bone tissues; a study of their structural properties and luminescence spectra. Synthesis of LaF$_3$:Tb$^{3+}$ was carried out by coprecipitation of components from aqueous and alcoholic (methanol) solution. As precursors were used: La(NO$_3$)$_3$$\times$6H$_2$O, TbCl$_3$, NH$_4$F. All reagents have qualification “chemically pure”. Distilled water and methanol were used as solvent. The synthesis of nanosized magnetite in the single-domain state was performed by the Elmore method. Synthesized nanodisperse samples are characterized by XRD analysis, DTGA, TEM. The magnetic properties and spectra of UV luminescence were also studied. It has been found that the XRD-patterns of LaF$_3$:Tb$^{3+}$ samples synthesized in water and methanol do not differ fundamentally. Under the experimental conditions, the most perfect crystals of hexagonal syngony were formed during crystallization in an autoclave. Their average size was ~ 15 nm. In TEM images, the length of the crystals exceeds the width by 3–4 times. Crystals are prone to aggregation and the formation of chain structures. The UV luminescence spectrum of the synthesized nanodisperse samples in aqueous medium at the concentration of 0.5 mg/ml and excited by ultraviolet radiation is characteristic of the structure of LaF$_3$:Tb$^{3+}$. Ensembles of particles Fe$_3$O$_4$/LaF$_3$:Tb$^{3+}$ NCs were synthesized. Transmission electron microscopy has shown that the shapes of particles of NCs and LaF$_3$:Tb$^{3+}$ nanocrystals are fundamentally different. Particles of Fe$_3$O$_4$/LaF$_3$:Tb$^{3+}$ NCs have a spherical shape, which is characteristic of structures of the core-shell type. X-ray diffraction patterns of NCs confirm this conclusion. The conditions for the synthesis of NCs did not significantly change the magnetic properties of their nuclei, single-domain Fe$_3$O$_4$ nanoparticles (NPs). The luminescence spectrum of Fe$_3$O$_4$/LaF$_3$:Tb$^{3+}$ NCs differs significantly from the spectrum of samples of nanodispersed LaF$_3$:Tb$^{3+}$ both in intensity and in the structure of the bands. These spectral differences may be due to differences in structure, features of the nanocrystalline structure, the content of the LaF$_3$:Tb$^{3+}$ scintillator and Tb$^{3+}$ ions in samples of LaF$_3$:Tb$^{3+}$ nanocrystals and shells of Fe$_3$O$_4$/LaF$_3$:Tb$^{3+}$ nanocomposites. Composites of dispersed 60S bioglass with nanodispersed crystalline LaF$_3$:Tb$^{3+}$ in the dry state, and distilled water, showed the presence of luminescence upon excitation by UV radiation. The results of research show the prospects of the synthesized nanodispersed luminophors LaF$_3$:Tb$^{3+}$, for use as a source of luminescent radiation in optopharmacology and photodynamic therapy of tumors in organs of cranial cavity and bone tissues. Optimization of luminescent properties of the original nanodispersed luminophors, their compositions with bioactive glass, luminescent shells in the composition of magnetosensitive NCs, as well as the technology of manufacturing of these structures will significantly allow us to improve their performance characteristics. The results of the work indicate the prospects of the synthesized structures for further research under the conditions of excitation by high-permeability “soft” X-ray radiation for use in optopharmacology and photodynamic therapy of tumors in organs of cranial cavity and bone tissues. Optimization of properties of the original nanodispersed luminophors, their compositions with bioactive glass and magnetosensitive carriers Fe$_3$O$_4$ will allow us to improve significantly their performance characteristics.

Keywords: nanodisperse luminophors, lanthanum fluoride, nanocomposites, magnetite, bioglass
INTRODUCTION

The problem of creating multifunctional drugs for targeted delivery with dosed local release of bioactive components is relevant in many areas of modern medicine. Thus, for oncology, the development of the concept of chemical construction of magnetosensitive nanocomposites (NCs) of the core-shell type with a multilevel hierarchical layered shell nanoarchitecture capable of performing the functions of medical-biological nanorobots: recognition of specific cells, viruses and biomacromolecules in biological media; targeted delivery and deposit of drugs in cells and target organs; combined local chemotherapeutic and osteoconductive drugs with prolonged action for topical use is a priority [6]. When using topical drug release, there are difficulties associated with the fixation and subsequent removal of the implant, which can cause additional stress on the body. From this point of view, bioactive ceramics, in particular different types of sol-gel glass, have an undeniable advantage over many other drug carriers because they are biocompatible, do not cause a negative immune response, are quickly and reliably fixed due to direct biochemical interaction with adjacent tissues, do not encapsulated with the formation of connective tissue (which is characteristic of foreign materials), as well as gradually biodegradable in the body by resorption and biochemical reactions [7–9]. A significant advantage of bioceramic materials is their capability to introduce into them the necessary substances in order to expand their functional properties and improve efficiency. In particular, in recent years, the efforts of researchers in this field are aimed at introducing a method of photodynamic therapy (PDT), which can be used for minimally invasive treatment of malignant tumors localized in soft tissues and in hard to reach places, such as organs of cranial cavities, bone structures, etc. [10].

It is known that PDT – a method of treatment based on the use of photosensitive substances, photosensitizers, is used in oncology, as well as in the treatment of certain skin diseases and infectious diseases [11–14]. Traditionally, the photosensitizer (PS) is administered intravenously, but can also be used by application or orally. PS for PDT selectively accumulates in the tumor or other pathologically affected target tissues or cells, after which they are irradiated with light with a wavelength corresponding to the maximum absorption of PS. Lasers that emit light of the desired wavelength and sufficient intensity are used as the light source. The uptake of light quanta by photosensitizer molecules in the presence of oxygen leads to a photochemical reaction, as a result of which molecular triplet oxygen is converted into singlet oxygen, and a large number of highly active radicals are formed. Singlet oxygen and radicals cause apoptosis and/or necrosis in tumor cells. In addition, PDT leads to the death of the tumor due to damage of its microvessels.

New approaches that may be useful for treatment, in particular minimally invasive, malignant tumors localized in the cranial organs, bone tissue, etc., may be photodynamic therapy and optopharmacology. These methods are based on the use of magnetically sensitive carriers for targeted delivery of drugs, modern bioceramic osteoconductive materials and highly efficient biocompatible nanosized luminophors with specified spectral characteristics of absorption and luminescence, safe for human body photosensitizers and high-permeable "soft" X-ray radiation [14–17].

At this time in the Chuiko Institute of Surface Chemistry of National Academy of Sciences of Ukraine there is developed and studied a wide class of nanosized magnetically sensitive materials: metal particles Fe, Co, Ni, single-domain ferrites Fe3O4, MnFe2O4, NiFe2O4, CoFe2O4, GdFe2O4, solid solutions in systems (Fe1–xMnx)Fe2O4, (Fe1–xNix)Fe2O4, (Fe1–xCox)Fe2O4, (Fe1–xZnx)Fe2O4) [18]. By changing their type and varying the chemical composition, it is possible to meet many requirements that arise when creating NCs for biomedical, environmental and technical applications with a given set of properties. It should be noted that nanosized one-domain magnetite (Fe3O4) has become especially widely used, in particular, for medical purposes [14]. It is known that magnetite has a biogenic
nature, and its unique properties, methods of manufacture, surface modification, creation of magnetic fluids based on Fe₃O₄, are well studied. Therefore, magnetite has become one of the most promising materials for the manufacture of multifunctional drug carriers with optimal properties and NCs.

At the I.M. Frantsevich Institute of Problems of Materials Science of the National Academy of Sciences of Ukraine, a new generation of highly effective bioactive ceramics was created, the peculiarities of their properties were studied, and the results of clinical applications were analyzed at Bogomolets National Medical University [19, 20]. Bioceramic materials have been used to develop new nanocomposites with antitumor drugs [6].

The list of photosensitizers that have been tested in clinical trials and are most widely known as photodynamic drugs includes: a derivative of benzoporphyrin – verteporfin; ethylthiopurpurin tin – puritin; Lu-Tex – tetraxphin lutetium; hematoporphyrin derivatives and sodium porfimer (Photofrin), etc. [11]. In addition, at this time there are many organic compounds that are promising for use as photosensitizers, which are at the stage of laboratory research [14–17].

Based on the focus of the work on the synthesis and study of the properties of nanodispersed luminophors for photodynamic therapy of tumors of the cranial cavity and bone tissues, promising for research may be X-ray luminescent nanosized LaF₃ particles doped with ions of rare earth elements, obtained by the technology of co-precipitation with aqueous solutions [15–17]. Their research, at least at the initial stage, in order to optimize the synthesis technology, it is advisable to conduct using ultraviolet (UV) radiation, which is much easier and safer to work with than X-ray.

Therefore, the aim of this work is the synthesis of nanostructures based on lanthanum fluoride, promising for use in photodynamic therapy of tumors in organs of cranial cavity and bone tissues; study of their structural properties and luminescence spectra.

MATERIALS AND METHODS OF RESEARCH

Synthesis of nanodispersed LaF₃:Tb³⁺.

Synthesis of nanodispersed luminophor LaF₃:Tb³⁺, was carried out by coprecipitation of components from aqueous and alcoholic (methanol) solution [15, 16]. As precursors were used: La(NO₃)₃×6H₂O, TbCl₃, NH₄F. All reagents have qualification “chemically pure”. Distilled water and methanol were used as solvent. Used for synthesis: 18.473 g La(NO₃)₃×6H₂O (42.664 mmol), 5.708 g TbCl₃ (10.769 mmol), 4.773 g NH₄F (127.992 mmol).

In order to obtain samples of LaF₃:Tb³⁺, the following variants of synthesis were developed.

1. La³⁺ and Tb³⁺ salts in molar ratios of 4:1 were successively dissolved in a minimum volume of distilled water (or methanol). With constant stirring, the solution was added dropwise with the content of F⁻ ions in the ratio La: F as 1:3. The reaction solution was stirred at room temperature for 2 hours. The product was centrifuged, washed three times with deionized water and dried at room temperature [21].

2. Components in the same ratios and sequences were introduced into the reactor and synthesized at 75 °C. An increase in temperature in this case leads to a relatively small increase in the size of the primary particles (~ 10–15 %), a decrease in the degree of aggregation and the formation of a more ordered crystal structure [21–23].

3. The LaF₃:Tb³⁺nanoparticles obtained in the coprecipitation process were transferred to an autoclave with programmed heating/cooling at a rate of 1 °C/min and kept at 150 °C for 24 hours. The obtained products were separated and washed twice with deionized water and dried at 60 °C. Treatment with elevated temperature and pressure leads to the disappearance of small crystals, the evolution of the shape of the base of the crystals to a hexagonal and the formation of a porous surface of the samples [24–27].

4. NCs Fe₃O₄/LaF₃:Tb³⁺ [29] in this work was synthesized as follows: first to wash with distilled water to pH = 7 source freshly synthesized magnetite [14] a solution of salts of La³⁺ and Tb³⁺ was added in the ratio of active hydroxyl groups on its surface to the number of La³⁺ ions as 1:1 (according to DTA, the concentration of hydroxyl groups on the surface of Fe₃O₄ was 2.2 mmol/g) and left for 24 hours for adsorption saturation of the surface. Then the salt solution was drained, the Fe₃O₄ particles with adsorbed La³⁺ and Tb³⁺ were washed three times into 50 ml of deionized water. After that, with constant stirring, the solution was added dropwise with the content of F⁻ ions in the ratio La: F as 1:3 (it is assumed that all ions La³⁺ and Tb³⁺ are

ISSN 2079-1704, ХФТП 2021. Т. 12. № 3
adsorbed on the surface of Fe3O4). The obtained NCsFe3O4/LaF3:Tb3+ was washed with distilled water and dried at 60 °C. Note that the chosen method of synthesis of NCsFe3O4/LaF3:Tb3+ promotes the formation of their structure by the type of nucleus (Fe3O4) – shell (LaF3:Tb3+).

**Synthesis of nanosized Fe3O4.** Nanodisperse magnetite in the single-domain state was synthesized by the Elmore reaction [14].

**Synthesis of sol-gel bioglass (BG 60S).** The synthesis of bioglass (BG 60S) was carried out by the sol-gel method [6]. 60S glass has a composition (mol %) of 60 % SiO2, 36 % CaO, 4 % P2O5. The synthesis was carried out by sol-gel method using: tetraethyl orthosilicate (TEOS) (C2H5O)4Si, triethyl phosphate (TEF) (C2H5O)3PO, ethanol C2H5OH, calcium nitrate tetrahydrate (Ca(NO3)2×4H2O), 59 % solution of nitric acid (HNO3). Mass ratios of precursors for the synthesis of 60S glass were: (C2H5O)4Si : (C2H5O)3PO : (Ca(NO3)2×4H2O) : H2O : C2H5OH = 8.59 : 1 : 5.85 : 9 : 3.

**XRD analysis of samples.** Structural studies the obtained samples were performed by powder X-ray diffraction method (XRD) using a DRON-UM1 diffractometer (“Burevestnik”, Russia) with Fe filtered CoKα radiation, focusing on Bragg-Brentano, in 2θ range of 10–80°. The size of the crystallites was determined by the width of the corresponding most intense line according to the Scherer equation.

**Magnetic properties.** Hysteresis loops of the magnetic moment of the samples were measured using a laboratory vibrating magnetometer of the Foner type at room temperature. Demagnetized NP were distributed in paraffin matrix with a volume concentration ~ 0.05 to prevent aggregation. For comparison, we used materials with a known value of the specific saturation magnetization (σs): a tested sample of nickel and magnetite NP (98 %) manufactured by Nanostructured & Amorphous Materials Inc., USA. In relation to the reference sample, the measurement error σs did not exceed 2.5 %.

**DTGA study of samples.** Study of samples by differential thermal analysis (DTGA) was performed using a Q-1500D (IOM Hungary).

**TEM study of samples.** To study the morphology and size of NPs used their dispersions in aqueous-ethanol solution (Transmission Electron Microscope JEM-2100F, Japan).

**Study of luminescence of samples.** Excitation of the luminescence of the samples was carried out by radiation of the lamp DRSH-500, passed through a UV filter MidOptBP324.

**RESULTS AND DISCUSSION**

The results study of X-ray diffraction are shown in Fig. 1 a, b, c. It can be seen that the diffraction patterns of LaF3:Tb3+ samples synthesized (Fig. 1 a, b) in water and methanol do not differ fundamentally. Under the conditions of the experiments, the most perfect crystals were formed during crystallization in an autoclave. Their average size was ~ 15 nm. Lanthanum (III) fluoride forms colorless crystals of hexagonal syngony, spatial group P3c1, unit cell parameters a = 0.7186 nm, c = 0.7352 nm, Z = 6; insoluble in water; forms crystal hydrates of LaF3×0.5H2O composition.

Fig. 2 shows TEM images of LaF3:Tb3+ nanocrystals synthesized in an aqueous medium. It is seen that the length of the crystals exceeds the width by 3–4 times. Crystals are prone to aggregation and the formation of chain structures. Note that the advantage of the method of obtaining a nanoscintillators in aqueous and in alcoholic environment is the capability to combine in a single process the synthesis of nanocomposite magnetic fluids and bioactive ceramic materials based on phosphates and silicates, with a content of LaF3:Tb3+.

The luminescence spectrum of a sample of nanodispersed LaF3:Tb3+, when diluted in water at the concentration of 0.5 mg/ml and when excited by ultraviolet radiation (Fig. 3 curve 1), shows bands characteristic of the structure of LaF3:Tb3+ [15, 16]. For comparison, the luminescence spectrum of an undoped LaF3 sample under the same conditions is given (curve 2).

The synthesized NPs Fe3O4 in the original ensemble were characterized by sizes 3–23 nm and a single-domain state. An ensemble of NPs with an average size of 11 nm was used in this work. The specific surface area of the synthesized magnetite was S_p = 105 m²/g. Magnetite was characterized by a coercive force Hc = 55.0 E, specific saturation magnetization σs = 56.2 Gs·cm³/g, relative residual magnetization Mr/Ms = 0.2 and can be used as a magnetically sensitive carrier for targeted delivery of drugs and biologically active compounds.

For the TEM image of the ensemble of particles of NCsFe3O4/LaF3:Tb3+ is characterized.
by a fundamental difference in the structure of particles from the structure of nanocrystals LaF₃:Tb³⁺ (Fig. 2a) – close to spherical, which is characteristic of NCs core-shell type (Fig. 4). X-ray diffraction patterns (Fig. 5) confirm the conclusion about the formation of the structure of the core-shell type NCsFe₃O₄/LaF₃:Tb³⁺. Note that the conditions for the synthesis of NCs did not significantly change the magnetic properties of their nuclei - single-domain NPs Fe₃O₄.

Fig. 1. XRD patterns of LaF₃:Tb₃ samples synthesized in water (a), methanol (b) and in an autoclave (c)

Fig. 2. TEM images of LaF₃:Tb⁺ nanocrystals: a – scale bar 20 nm; b – scale bar 50 nm; c – scale bar 100 nm; d – scale bar 1000 nm
The luminescence spectrum of NCs Fe₃O₄/LaF₃:Tb³⁺ (Fig. 6) differs significantly from the spectrum of samples of nanodispersed LaF₃:Tb³⁺ (Fig. 3, curve 1) both in intensity and in the structure of the bands. These spectral differences may be due to differences in structure, features of the nanocrystalline structure, the content of the LaF₃:Tb³⁺ scintillator and Tb³⁺ ions in it (Fig. 3, curve 1) in shells of NCs Fe₃O₄/LaF₃:Tb³⁺ (Fig. 6, curve 1).

**Fig. 3.** Luminescence spectrum of nanodispersed samples LaF₃:Tb³⁺ (1) and LaF₃ (2) dilution 0.5 mg/ml

**Fig. 4.** TEM images of NCs Fe₃O₄/LaF₃:Tb³⁺; scale bar 20 nm

**Fig. 5.** XRD patterns of NCs Fe₃O₄/LaF₃:Tb³⁺
In conclusion, the composites of dispersed bioglass 60S and nanodispersed crystalline LaF$_3$:Tb$^{3+}$ in the dry state, and in distilled water, showed the presence of luminescence when excited by UV radiation, which indicates the possibility of their use in photodynamic therapy of bone cancer.

These data indicate the achievement of the goal of this work. In the future, the optimization of the luminescent properties of the original nanodisperse luminophors, their compositions with bioactive glass, luminescent shells in the composition of magnetically sensitive NC, as well as the technology of manufacturing these structures. We hope that this will significantly improve their performance, create the prospect of use in photodynamic therapy and optopharmacology as sources of luminescent radiation and drug carriers, both individually and as part of various types of nanocomposites.

**CONCLUSIONS**

Nanodispersed luminophors of LaF$_3$:Tb$^{3+}$ type were synthesized, promising for use as a source of luminescent radiation both in individual application and as a part of nanocomposites of different types; their structural properties and luminescence spectra during UV excitation were studied. Diffractograms of the samples of LaF$_3$: Tb$^{3+}$ synthesized in water and methanol are not fundamentally different. Under the experimental conditions, the most perfect crystals of hexagonal syngony were formed during crystallization in an autoclave. Their average size was ~ 15 nm. The length of TEM images of crystals exceeds the width by 3–4 times. Crystals are prone to aggregation and the formation of chain structures. The UV luminescence spectrum of the synthesized nanodisperse samples upon excitation by ultraviolet radiation is characteristic of LaF$_3$:Tb$^{3+}$.

Ensembles of Fe$_3$O$_4$/LaF$_3$:Tb$^{3+}$ NC particles with a core-shell type structure were synthesized. The conditions for the synthesis of NCs did not significantly change the magnetic properties of their nuclei, single-domain Fe$_3$O$_4$ NP. The luminescence spectrum of Fe$_3$O$_4$/LaF$_3$:Tb$^{3+}$ NCs differs significantly from those of the samples of nanodispersed LaF$_3$:Tb$^{3+}$ both in intensity and in the structure of the bands. These spectral differences are probably due to differences in nanocrystalline structure, content of Tb$^{3+}$ ions, etc. in samples of LaF$_3$:Tb$^{3+}$ nanocrystals and shells of Fe$_3$O$_4$/LaF$_3$:Tb$^{3+}$ nanocomposites.

The composites of dispersed bioglass 60S with nanodispersed crystalline LaF$_3$:Tb$^{3+}$ in the dry state, and in distilled water, showed the presence of luminescence when excited by UV radiation.

The results of the work indicate the prospects of the synthesized structures for further research under the conditions of excitation by high-permeability “soft” X-ray radiation for use in optopharmacology and photodynamic therapy of tumors in organs of cranial cavity and bone tissues. Optimization of properties of the original nanodispersed luminophors, their compositions with bioactive glass and magnetosensitive carriers Fe$_3$O$_4$ will allow us to improve significantly their performance characteristics.
Синтез та властивості наноструктур на основі фториду лантану для фотодинамічної терапії пухлини захворювань органів черепної порожнини та кісткових тканин

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Метою роботи є синтез наноструктур на основі фториду лантану, перспективних для застосування в фотодинамічній терапії пухлинних захворювань органів черепної порожнини та кісткових тканин; дослідження їх структурних та спектральних властивостей та спектрів люмінесценції. Синтез LaF₃:Tb⁺³ здійснено співосадженням компонентів із водяного та спиртового (метанол) розчину. Як прекурсори використано: La(NO₃)₃·6H₂O, TbCl₃, NH₄F. Всі реактиви кваліфіковані «х.ч.». Як розчинник використано дистильовану воду, метанол. Синтез нанорозмірного магнетиту в однодоменному стані виконували методом Елмора. Синтезовані нанодисперсні зразки були охарактеризовані методами рентгенівської дифракції, диференційного термогравіметричного аналізу, просвічувальної електронної мікроскопії. Виявлено також магнітні властивості і спектри УФ-люмінесценції. Вивчено, що дифрактограми зразків LaF₃:Tb⁺³, синтезованих у середовищі води і метанолу, принципово не різняться. В умовах експерименту найбільш досконалі кристали гексагональної сингонії утворювалися при кристалізації в автоклавах. Їхні середній розмір становить ~ 15 нм. Довжина ПЕМ-зображення кристалів LaF₃:Tb⁺³ перевищує ширину в 3–4 рази. Кристали складні до агрегації та утворення ланцюжкових структур. Спектр УФ-люмінесценції синтезованих нанодисперсних зразків в середовищі води в концентрації 0.5 ml/ml та досліджувані ультрафіолетовим випромінюванням, характерним для структури LaF₃:Tb⁺³. Синтезовано ансамбль частинок НК Fe₃O₄/LaF₃:Tb⁺³. Методами просвічувальної електронної мікроскопії встановлено, що форма частинок НК і нанокристалів LaF₃:Tb⁺³ принципово відрізняються. Частинки НК Fe₃O₄/LaF₃:Tb⁺³ мають кубичну форму, що характерно структурі групи здвоєння оболонок. Рентгенівські дифрактограми НК підтверджують цей висновок. Умови синтезу НК інші, що змінюють магнітні властивості їхніх ядер – однодоменних НЧ Fe₃O₄. Спектри люмінесценції НК Fe₃O₄/LaF₃:Tb⁺³ інші, що відрізняються від спектрів зразків нанодисперсних LaF₃:Tb⁺³ як за інтенсивністю, так і за структурою смуг. Вказані спектральні відмінності можуть бути обумовлені відмінностями ядерного стану, особливостями нанокристалічної структури, вмістом цинкітовиця LaF₃:Tb⁺³ та іонів Tb⁺³ в зразках нанокристалів LaF₃:Tb⁺³ та оболонках нанокомпозитів Fe₃O₄/LaF₃:Tb⁺³. Композит дисперсованого біоска 60% з нанодисперсним кристалічним LaF₃:Tb⁺³ в схему стані та середовищі дистильованої води демонстрували наявність люмінесценції при збудженні УФ-випромінюванням. Результати роботи свідчать про відмінності синтезованих структур для подальших досліджень в умовах біологічного випромінювання в місцях рентгенівським випромінюванням з метою їхнього використання в протифармацевтичні та фотодинамічні терапії пухлинних захворювань органів черепної порожнини та кісткових тканин. Оптимізація властивостей викладених нанодисперсних люмінофорів, їхніх композицій з біоактивним склом та магніточутливою носією Fe₃O₄ дозволить істотно покращити експлуатаційні характеристики.

Ключові слої: нанодисперсні люмінофори, фторид лантану, нанокомпозити, магнетит, біоцемент

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Received 01.07.2021, accepted 01.09.2021