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A.P. Kusyak [1], A.L. Petranovska [1], S.P. Turanska [1], O.I. Oranska [1], Ya.M. Shuba [2], D.I. Kravchuk [2], L.I. Kravchuk [2], V.G. Nazarenko [3], R.M. Kravchuk [3], V.A. Dubok [4], V.S. Chornyi [5], O.A. Bur'yanov [5], Yu.L. Sobolevs'kyy [5], P.P. Gorbyk [1]

SYNTHESIS, PROPERTIES AND APPLICATION POSSIBILITIES OF X-RAY LUMINESCENT NANOCRYSTALLINE LANTHANUM PHOSPHATE

[1] Chuiko Institute of Surface Chemistry of National Academy of Sciences of Ukraine
17 General Naumov Str., Kyiv, 03164, Ukraine, E-mail: phorbyk@ukr.net
[2] Bogomoletz Institute of Physiology of National Academy of Sciences of Ukraine
4 Bogomoletz Str., Kyiv, 01601, Ukraine
[3] Institute of Physics of National Academy of Sciences of Ukraine
46 Nauky Aven., Kyiv, 03028, Ukraine
[4] Frantsevich Institute of Problems of Materials Science of National Academy of Sciences of Ukraine
3 Akademika Krzhyzhanovskoho Str., Kyiv, 03142, Ukraine
[5] Bogomolets National Medical University
13 Taras Shevchenko Blvd., Kyiv, 01601, Ukraine

The purpose of the work is the synthesis of samples of X-ray luminescent nanodispersed lanthanum phosphate activated with terbium ($LaPO_4:Tb^{3+}$), the study of their structural properties and luminescence spectra when excited by ultraviolet and X-ray radiation, as well as determination of the possibility of their use in nanocomposites with bioactive glass and colloidal nanosystems. Samples of nanocrystalline lanthanum phosphate were synthesized composed of $LaPO_4 \cdot 0.5H_2O$, of hexagonal syngonium, activated with terbium, their structural properties, luminescence spectra were studied upon excitation by UV and X-ray radiation, a possibility was shown to use them in nanocomposites with bioactive sol-gel glass and aqueous colloidal systems. Composites of 60S bioglass with nanodispersed crystalline $LaPO_4:Tb^{3+}$ in the dry state and in distilled water medium demonstrated the presence of luminescence when excited by UV and X-ray radiation. The given data indicate the perspective of nanodispersed phosphors based on lanthanum phosphate, their composites with bioactive sol-gel glass in colloidal systems, for use in optopharmacology and photodynamic therapy of diseases localized in bone tissues. In addition, the results of research can be useful for technical applications, in particular, in the creation of luminescent detectors of high-energy electromagnetic radiation, development of photo- and optoelectronic devices, etc.

***Keywords**: lanthanum phosphate, nanodispersed crystals, activation, terbium, bioactive glass, nanocomposites, colloidal nanosystems, X-ray luminescence*

INTRODUCTION

With the development of nanotechnology in the 21st century, the efforts of many researchers are directed to the creation and introduction into clinical medicine of the latest effective multifunctional remedies for targeted delivery and local therapy with prolonged release of bioactive components [1–9]. The introduction of the indicated remedies in the fields of photopharmacology and photodynamic therapy (PDT) has become a particularly urgent task using highly effective biocompatible nanosized X-ray phosphors and photosensitizers with specified spectral characteristics in the clinical minimally invasive treatment of malignant tumor formations localized both in deeply placed soft tissues and hard-to-reach bone structures, as well as in organs of skull [10–14].

As known [10–14], for the implementation of X-ray photodynamic therapy (XRPDT), in particular, according to the improved method of PDT using X-ray radiation, a photopharmacological agent is required based on a non-toxic and biocompatible nanodispersed phosphor, which is excited by X-ray radiation and emits visible light with a wavelength necessary for the effective operation of the photosensitizer (for example, in the green, red or infrared range of spectrum).

Our paper [14] reported on the synthesis of terbium-activated nanocrystalline samples of lanthanum fluoride of hexagonal syngonium, the results of studying their structural properties and

X-ray luminescence, and showed the possibility of their use as part of nanocomposites with magnetically sensitive nanosized drug carriers and bioactive sol-gel glass. The given data indicate the promising nature of these nanostructures for further research with the aim of using them in optopharmacology and photodynamic therapy of tumor diseases. In addition, research results can be useful for technical applications, in particular, in the creation of luminescent detectors of high-energy electromagnetic radiation, development of photo- and optoelectronic devices, *etc*.

However, for the treatment of diseases localized in organs of skull and bone tissues, the most suitable are phosphors based on phosphates [15], activated by rare earth elements, characterized by effective X-ray luminescence with a maximum of 530–560 nm when excited by highly penetrating "soft" biologically safe X-ray radiation, which is used in medicine for diagnostic and therapeutic purposes in the treatment of oncological diseases of bones and tumors localized in organs of skull. Phosphates are non-toxic compounds, biocompatible with bone tissues, suitable for use in PDT [16–18], which gives them certain advantages, for example, compared to fluorides. As part of bioactive ceramics, they are widely used in the treatment of various bone diseases. The use of phosphate in the research of this work is mainly due to its biosafety when interacting with bone tissues.

Therefore, the aim of this work was to synthesize samples of X-ray luminescent nanodispersed lanthanum phosphate activated with terbium ($LaPO_4:Tb^{3+}$), to study their structural properties and luminescence spectra upon excitation by ultraviolet (UV) and X-ray radiation, to determine the possibility of their use as part of nanocomposites with bioactive glass and colloidal nanosystems.

EXPERIMENTAL PART

Research materials and methods. The synthesis of samples of nanodispersed phosphors $LaPO_4:Tb^{3+}$ was carried out by coprecipitation from salt solutions. The following precursors were used: $La(NO_3)_3{\cdot}6H_2O$, $TbCl_3{\cdot}6H_2O$, $NH_4H_2PO_4$. All used reagents were qualified as "chemically pure". Deionized water or methanol were used as a solvent.

Synthesis of $LaPO_4:Tb^{3+}$ was performed at room temperature. La^{3+} and Tb^{3+} salts in molar ratios of 3:1.1 were successively dissolved in 100 mL of deionized water (methanol). It was taken: 0.13 g of $La(NO_3)_3{\cdot}6H_2O$ (3.0 mmol), 0.041 g of $TbCl_3$ (1.1 mmol), 0.049 g of $NH_4H_2PO_4$ (4.1 mmol) per 100 mL of solution. A solution of PO_4^{3-} ions was added dropwise to the mixture of salts, with constant stirring, for 2 h, in the ratio of $La^{3+} : PO_4^{3-}$ as 3 : 4.1 (mmol). A finely dispersed white precipitate is formed. The product was centrifuged, washed three times with deionized water (methanol) and dried at room temperature. The used load of reagents ensured the composition of the synthesized samples corresponding to the formula $La_xTb_{1-x}PO_4$, $x = 0.8$.

X-ray diffractograms of the samples were recorded on a DRON-4-07 diffractometer (NVO Burevisnyk, St. Petersburg, Russia) in filtered CuK_α radiation with the Bragg-Brentano shooting geometry in the angular range of 10–80 degrees with a step of 0.05 degrees and exposure at point 1 *s*. Phase identification was carried out using the X-ray database PDF-2. The average crystal size was determined according to the Scherrer equation.

Excitation of luminescence of the samples by UV rays was carried out by radiation of a DRSH-500 lamp, passed through a MidOpt BP324 UV filter.

The X-ray source of a powder diffractometer ARXD of Proto firm (CuK_α radiation, λ = 1.54056 Å) was used to excite X-ray luminescence of the experimental samples. X-ray luminescence spectra were measured using an Ocean Optics USB2000 spectrometer and OmniDriverCSharpDemo software. The analysis of the luminescence spectra was carried out by fitting certain areas of the spectra in accordance with the measured peaks by a Gaussian curve.

A fragment of the laboratory installation for studying of X-ray luminescence of synthesized samples is shown in Fig. 1. To excite luminescence, X-ray radiation from source *1* was directed at test sample *2*, placed on holder *3*, at an angle of 40° during all the time of measuring spectra (~300 *s*). The samples were irradiated under the following operating parameters of the X-ray source: U = 30 kV; I = 20 mA. X-ray luminescence spectra were measured with the following parameters: integration time of 10 s, averaging 30 times. The spectra were measured using the inserted into a diffractometer FC-UV-400-2 optical fiber with a collimator nozzle *4*. The distance from the particles of the

dispersed sample to the collimator was about 30 mm.

The X-ray luminescence was studied for a dry nanodispersed sample of $LaPO_4:Tb^{3+}$, a drop of distilled water, and a drop of a colloidal solution of $LaPO_4:Tb^{3+}/H_2O$ with $LaPO_4:Tb^{3+}$ concentration of 2.5 wt. %, placed on the surface of holder *3* (Fig. 1).

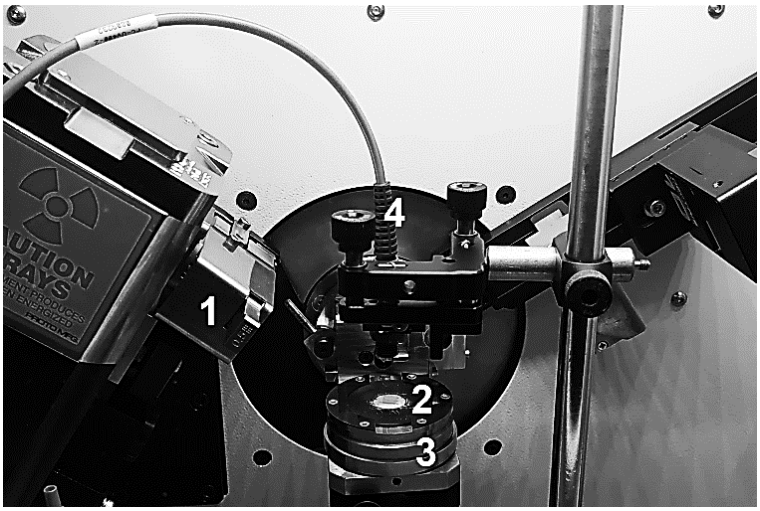


Fig. 1. Fragment of a laboratory installation for X-ray luminescence research of synthesized samples. *1* – X-ray source, *2* – sample, *3* – sample holder, *4* – optical fiber with a collimator nozzle

The size and shape of NPs were determined by electron microscopy using a transmission electron microscope (TEM) JEOL 1200 EX (Japan). The samples were prepared in the form of dispersions in deionized water, the drops were lowered onto a carbon-coated copper grid (EM Resolutions Ltd) and dried at room temperature for 12 h.

Samples were investigated by scanning electron microscopy (SEM) using a device JSM-6060 LA (JEOL, Japan).

The synthesis of sol-gel bioglass (BG 60S) was carried out according to the method [14]. 60S glass has a composition (mol. %): 60 % SiO_2, 36 % CaO, 4 % P_2O_5. During its synthesis by the sol-gel method, the following precursors were used: tetraethyl orthosilicate (TEOS) $(C_2H_5O)_4Si$, triethyl phosphate (TEP) $(C_2H_5O)_3PO$, ethanol C_2H_5OH, calcium nitrate tetrahydrate $(Ca(NO_3)_2{\cdot}4H_2O)$, 59 % solution of nitric acid (HNO_3) (all reagents of the "chemically pure" qualification (Merck Schuchardtohg (Germany)). The mass ratios of precursors for the synthesis of 60S BG were: $(C_2H_5O)_4Si$: $(C_2H_5O)_3PO$: $(Ca(NO_3)_2{\cdot}4H_2O)$: H_2O : C_2H_5OH = 8.59 : 1: 5.85 : 9 : 3. To obtain sol-gel glass, first TEOS, TEP, and ethanol are poured in the above proportions, mixed on a magnetic stirrer for 30 min, and then treated with ultrasound for 5 min. For hydrolysis and obtaining of a sol, nitric acid is added, the mixture is mingled again with the aid of a laboratory magnetic stirrer for 30 min, and treated again with ultrasound for 5 min. Separately an aqueous solution of calcium nitrate is prepared, mixing on a magnetic stirrer for at least 10 min. Then the solution of calcium nitrate is added to the sol, mixed on a magnetic stirrer for at least 40 min, sonicated for 5 min, and to complete the polycondensation processes, the sol is kept for 24 h at room temperature, and then warmed up in a closed container in a dry oven for 24 hours at 60 °C. The resulting gel is kept for at least 48 h at 120 °C, and then heated slowly (at least 4 h) to 900 °C and calcined at this temperature for 2 h.

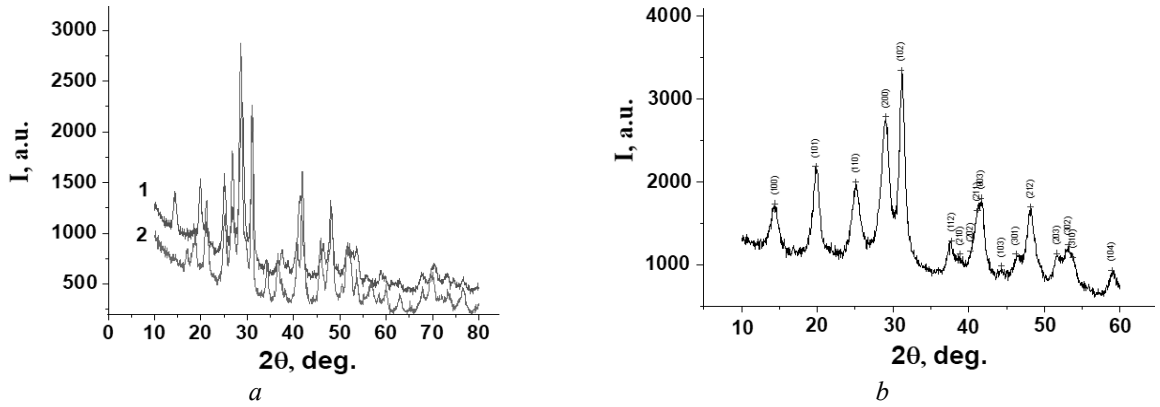
To obtain X-ray luminescent sol-gel glass, the method [14] was modified: after passing through TEOS and TEP hydration process, with constant stirring, a previously synthesized X-ray phosphor ($LaPO_4:Tb^{3+}$) was added, and the mixture was treated with ultrasound for 5 min. All other stages of the synthesis were carried out similarly to [14]. The amount of X-ray phosphor was ~1.5% (wt.) of the produced X-ray luminescent sol-gel glass.

Results and discussion. X-ray diffraction patterns of the reaction products $La(NO_3)_3$ and $NH_4H_2PO_4$ in a medium of water and methanol at 20 °C are shown in Fig. 2 *a*, curves *1*, *2*, respectively. The phase composition of the obtained products and their average size depend

on the conditions of their synthesis. Thus, crystals of $LaPO_4 \cdot 0.5H_2O$ phase were obtained in an aqueous medium, the average size of which was 24 nm (JCPDS 46-1439, 84-600). Crystals of $LaPO_4$ phase with the average size of 23 nm (JCPDS 84-600) were obtained in methanol.

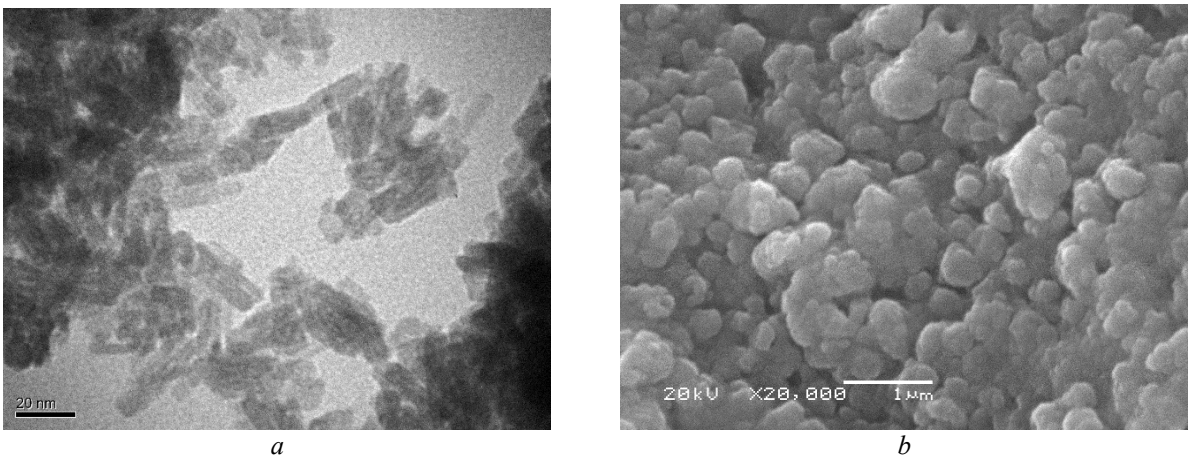
X-ray diffraction patterns of a typical $LaPO_4:Tb^{3+}$ sample synthesized in water medium at 20 °C are shown in Fig. 2 *b*. According to X-ray diffraction data, the synthesized terbium-activated lanthanum phosphate sample contains a single phase of $LaPO_4 \cdot 0.5H_2O$ of hexagonal syngonium with an average crystal size of 10 nm and a specific surface area of ~ 130 m^2/g. It should be noted that the average crystal size of $LaPO_4:Tb^{3+}$ samples can be controlled to a certain extent by changing the physicochemical parameters of the synthesis.

Fig. 3 shows TEM (*a*) and SEM (*b*) images of synthesized nanocrystalline $LaPO_4:Tb^{3+}$ samples, size scale of 20 nm (*a*) and 1 μm (*b*), respectively. It can be seen that the synthesized nanocrystalline samples of lanthanum phosphate are prone to aggregation.



a *b*

Fig. 2. *X*-ray diffractograms of typical reaction products $La(NO_3)_3$ and $NH_4H_2PO_4$ at 20 °C: *a* – in water (*1*) and methanol (*2*); *b* – a sample of $LaPO_4:Tb^{3+}$ synthesized in aquaous medium

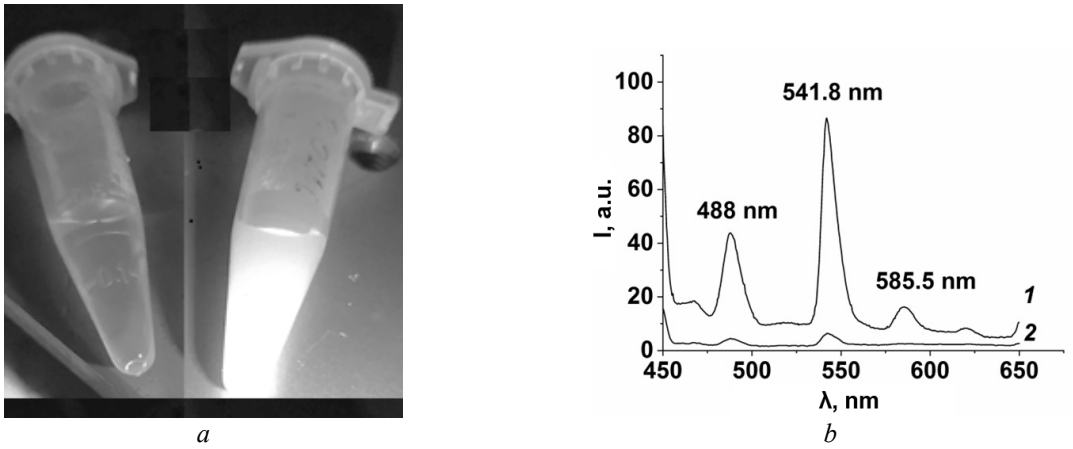


a *b*

Fig. 3. TEM (*a*) and SEM (*b*) images of typical $LaPO_4:Tb^{3+}$ samples. Size scale: 20 nm (*a*); 1 μm (*b*)

Fig. 4 shows the luminescence of a sample of nanodispersed $LaPO_4:Tb^{3+}$ in the state of an aqueous colloidal solution with a concentration of 2.5 wt. % upon excitation by UV radiation (365 nm). Fig. 4 *b* shows the UV-luminescence spectrum of the sample when diluted in distilled water at a concentration of 0.5 mg/mL (curve *1*). Curve *2* corresponds to the luminescence spectrum of $LaPO_4$ sample at a dilution of 0.05 mg/mL. It can be seen that the spectrum contains 4 main bands with maxima at 488; 541.8; 585.2; 622 nm, which can be associated with the corresponding electronic transitions involving the energy levels of Tb^{3+} ions in $LaPO_4$ band gap.

Fig. 5 shows a typical X-ray luminescence spectrum of nanodispersed $LaPO_4:Tb^{3+}$ samples. It can be seen that 4 characteristic X-ray luminescence bands are observed in the spectrum, the position of their maxima correlates with the corresponding bands upon excitation by UV radiation. This may indicate, in particular, that the mechanisms of UV and X-ray luminescence are close.



a *b*

Fig. 4. *a* – Luminescence of a sample of nanodispersed $LaPO_4:Tb^{3+}$ in the state of an aqueous colloidal solution with a concentration of 2.5 wt. % upon excitation by UV radiation (365 nm); *b* – UV-luminescence spectrum of the sample when diluted in water at epy concentration of 0.5 mg/mL (curve *1*). Curve *2* – at a dilution of 0.05 mg/mL. $T \sim 300$ K

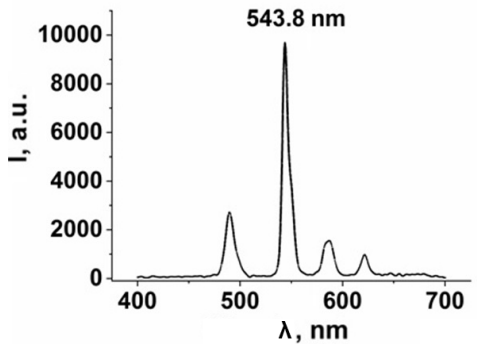


Fig. 5. Typical X-ray luminescence spectra of nanodispersed $LaPO_4:Tb^{3+}$ samples. $T \sim 300$ K

It should be noted that the optical spectra of Tb^{3+} ions in various dielectric matrices are currently well studied [10, 11, 19, 20]. In particular, it has been shown that the position of maximum of the luminescence bands of terbium-activated phosphors depends significantly on the chemical composition and structural properties of the matrix material, the way and conditions of excitation, *etc*. [21–23]. Thus, when exciting aqueous suspensions of $LaPO_4:Tb^{3+}$ nanocrystals by UV radiation, the luminescence bands characteristic of Tb^{3+} ions are observed in the visible area (Fig. 4 *b*). Due to the high values of the absorption coefficient of UV radiation, in this case, the surface area of $LaPO_4:Tb^{3+}$ nanocrystals is excited. X-ray radiation is characterized by significantly higher values of quantum energy and depth of penetration into a substance of matrix. Therefore, its interaction with the substance is accompanied by the intensive formation of dynamic and residual defects in the crystal structure of the matrix medium ($LaPO_4$ nanocrystals), which can, to a great extent, cause certain changes in the position of maxima of bands of X-ray luminescence spectra (Fig. 5).

Samples of nanostructured composites based on 60S bioglass and Tb^{3+}-activated lanthanum phosphate were synthesized. Dry samples of $60S:(LaPO_4:Tb^{3+})$ NC (insertions in Fig. 6 *a*, *b*) and their aqueous suspensions demonstrated the

presence of luminescence when excited by UV radiation.

Fig. 6 *a*, *b* show the X-ray luminescence spectra of nanostructured composites 60S:($LaPO_4$:Tb^{3+}) synthesized at 700 (insertion in Fig. 6 *a*) and 900 °C (insertion in Fig. 6 *b*), respectively. The presence of a band with a maximum at 545.1 nm may indicate that the X-ray luminescence may be related to the energy levels of Tb^{3+} activator. According to experimental data, an increase in the temperature of synthesis of 60S:($LaPO_4$:Tb^{3+}) composite to 900 °C contributes to the growth and redistribution of X-ray luminescence intensity of the composite in the bands of 545.1 and 488 nm.

Fig. 7 shows the X-ray luminescence spectrum of a typical colloidal solution based on distilled water and synthesized $LaPO_4$:Tb^{3+} nanocrystals. The good coincidence of the shape of X-ray luminescence spectra and their maxima for 60S:($LaPO_4$:Tb^{3+}) NC (Fig. 6) and $LaPO_4$:Tb^{3+} nanocrystals in the aqueous colloidal system $LaPO_4$:Tb^{3+}/H_2O (Fig. 7) indicates that in both cases the X-ray luminescence mechanism can be explained by the presence of the same center - the Tb^{3+} ion in $LaPO_4$ matrix. We should also note that the use of liquid media containing X-ray luminescent $LaPO_4$:Tb^{3+} nanocrystals have a perspective for the creation of new types of drugs with remotely controlled properties.

The given data indicate the potential of research into nanodispersed phosphors based on lanthanum phosphate, their composites with bioactive glass and colloidal systems, for use in optopharmacology and photodynamic therapy of bone tissue diseases.

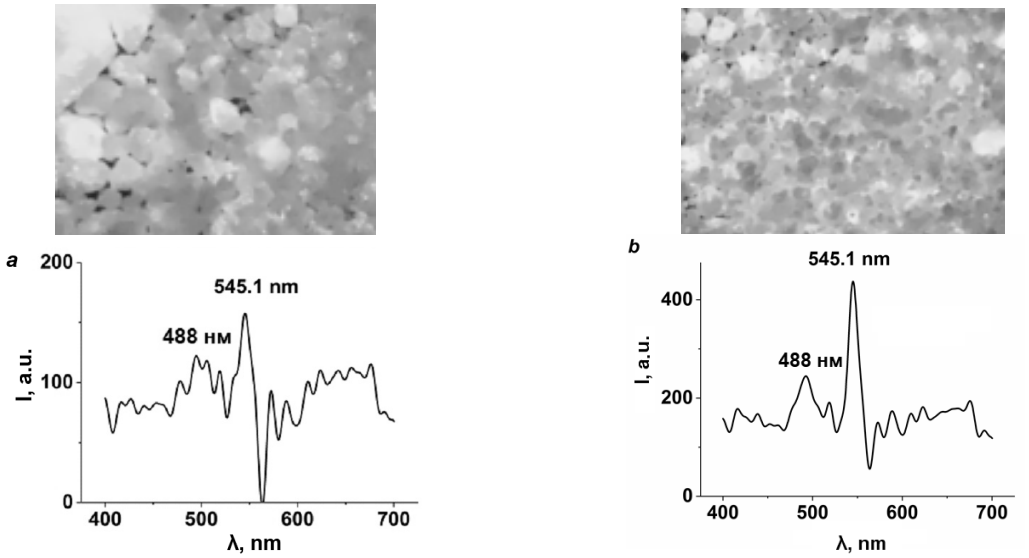


Fig. 6. UV luminescence (in insertions) and X-ray luminescence spectra of samples of 60S:($LaPO_4$:Tb^{3+}) composites synthesized at: *a* – 700 and *b* – 900 °C

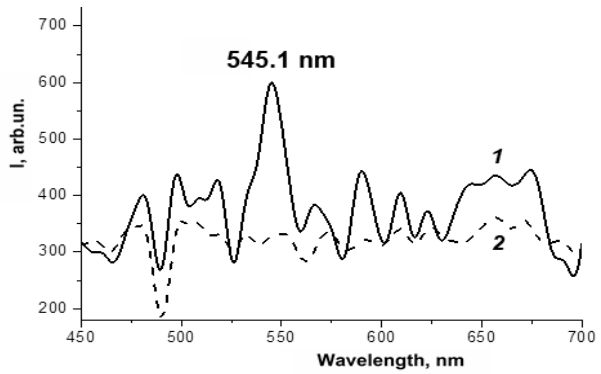


Fig. 7. Typical X-ray luminescence spectra of a colloidal solution: *1* – $LaPO_4$:Tb^{3+}/H_2O with $LaPO_4$:Tb^{3+} concentration of 2.5 mass %; *2* – distilled water. $T \sim 300$ K

CONCLUSIONS

Samples of nanocrystalline lanthanum phosphate composed of $LaPO_4 \cdot 0.5H_2O$, of hexagonal syngonium, activated with terbium were synthesized, their structural properties, luminescence spectra upon excitation by UV and X-ray radiation were studied, a possibility was shown to use them in nanocomposites with bioactive sol-gel glass and colloidal systems. Composites of 60S bioglass with nanodispersed crystalline $LaPO_4:Tb^{3+}$ in the dry state and in distilled water medium demonstrated the presence of luminescence when excited by UV and X-ray radiation. The given data indicate the potential of nanocrystalline phosphors based on lanthanum phosphate, their composites with bioactive sol-gel glass and colloidal systems, for use in optopharmacology and photodynamic therapy of diseases localized in bone tissues. In addition, research results can be useful for technical applications, in particular, in the creation of luminescent detectors of high-energy electromagnetic radiation, development of photo- and optoelectronic devices, *etc*.

Синтез, властивості та можливості застосування рентгенолюмінесцентного нанокристалічного фосфату лантану

А.П. Кусяк, А.Л. Петрановська, О.І. Оранська, С.П. Туранська, Я.М. Шуба, Д.І. Кравчук, Л.І. Кравчук, В.Г. Назаренко, Р.М. Кравчук, В.А. Дубок, О.А. Бур'янов, В.С. Чорний, Ю.Л. Соболевський, П.П. Горбик

Інститут хімії поверхні ім. О.О. Чуйка Національної академії наук України
вул. Генерала Наумова, 17, Київ, 03164, Україна, phorbyk@ukr.net
Інститут фізіології ім. О.О. Богомольця Національної академії наук України
вул. Академіка Богомольця, 4, Київ, 01601, Україна
Інститут фізики Національної академії наук України
Проспект Науки, 46, Київ, 03028, Україна
Інститут проблем матеріалознавства ім. І.М. Францевича Національної академії наук України
вул. Кржижанівського, 3, Київ, 03142, Україна
Національний медичний університет ім. О.О. Богомольця
бул. Тараса Шевченка, 13, Київ, 01601, Україна

Мета роботи – синтез зразків рентгенолюмінесцентного нанодисперсного фосфату лантану, активованого тербієм ($LaPO_4:Tb^{3+}$), вивчення їхніх структурних властивостей і спектрів люмінесценції при збудженні ультрафіолетовим та рентгенівським випромінюванням, а також встановлення можливості їхнього використання в складі нанокомпозитів з біоактивним склом і колоїдних наносистем.

Синтезовано зразки нанокристалічного фосфату лантану складу $LaPO_4 \cdot 0.5H_2O$, гексагональної сингонії, активовані тербієм, вивчено їхні структурні властивості, спектри люмінесценції при збудженні УФ- та рентгенівським випромінюванням, показано можливість використання в складі нанокомпозитів з біоактивним золь-гель склом, водних колоїдних систем. Композити біоскла 60S з нанодисперсним кристалічним $LaPO_4:Tb^{3+}$ в сухому стані та середовищі дистильованої води демонстрували наявність люмінесценції при збудженні УФ- та рентгенівським випромінюванням. Наведені дані свідчать про перспективність нанодисперсних люмінофорів на основі фосфату лантану, їхніх композитів з біоактивним золь-гель склом, у колоїдних системах, для використання в оптофармакології та фотодинамічній терапії захворювань, локалізованих у кісткових тканинах. Крім того, результати досліджень можуть бути корисними для технічних застосувань, зокрема, при створенні люмінесцентних детекторів високоенергетичного електромагнітного випромінювання, розробках фото- та оптоелектронних приладів тощо.

***Ключові слова**: фосфат лантану, нанодисперсні кристали, активація, тербій, біоактивне скло, нанокомпозити, колоїдні наносистеми, рентгенолюмінесценція*

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