Nanoluminofors based on silicates and germanates of rare earth elements for visualization of biotissues

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Abstract
Nanoparticles of silicates and germanates with a general formula Sr2R8-x2-x2Er3+,Yb3+M6O26 (R = Y, La; M = Si, Ge) were produced in vacuum by the method of pulse electron beam evaporation. An upconversion photoluminescence of the nanoparticles was detected during the excitation by a laser with a wavelength of 980 nm with a predominance of lines in the red and near infrared regions of the spectrum. Due to their optical properties, the nanoparticles can be excited directly through the biotissues to visualize various pathologies. The obtained nanosamples have K-jumps of X-ray radiation absorption in the 10–100 keV energy region. This opens up prospects for the use of the nanoparticles as X-ray contrast agents. Thus, the nanoparticles have both optical and X-ray contrast characteristics, and therefore have the potential necessary for imaging and diagnosing pathologies in biological tissues.

Keywords
Er3+, Yb3+
upconversion nanoluminophores biotissues bimodal substances

Key findings
• Silicates and germanates of rare earth elements are promising for visualization of biological tissues.
• Upconversion silicate and germanate nanoluminophores containing Er and Yb ions can be used for optical and X-ray bioimaging.

1. Introduction
Single-mode nanoparticles (NP) with optical or magnetic characteristics are widely used in biosensing and biovisualization [1]. However, they do not provide all the necessary information about biological objects. The requirements of modern biomedical technology suggest the development of new, multimodal bioprobes. Multimodal bioprobes combining two or more functions are emerging advances in biology and medicine. A number of nanomaterials with such interesting properties have found various biomedical applications, including imaging, separation, and drug delivery [2]. Inorganic nanoparticles doped with Ln3+ ions are considered good candidates for multimodal bioapplications, since they have unusual optical and magnetic properties [3]. Narrow width of f-f emission lines, long lifetime of photoluminescence (PL), IR excitation in the field of transparency of biological tissues (700–1000 nm), large antistox shifts for separation of upconversion photoluminescence (UCPL) from excitation, weak background of intrinsic luminescence of biotissues, low cytotoxicity, high chemical resistance and resistance to photobleaching make them extremely suitable for use in various bio-applications [4–7]. The increased intensity of red radiation could be useful for various UCPL applications, especially for deep tissue imaging [4]. Currently, magnetic resonance imaging (MRI), computed tomography (CT) positron emission tomography (PET), optical imaging, and other methods provide vivid tissue imaging; however, they cannot provide comprehensive information in clinical practice. Therefore, various multimodal imaging technologies have attracted considerable attention [8–11].

In this work, UCPL was studied and the dependencies of mass coefficients of weakening of X-ray radiation on the radiation energy for the nanopowders (NPs) produced by
3. Results and Discussion

Figure 1 shows the results of NPs microscopy based on solid solutions of Sr2La7.85Er0.075Yb0.075GeO26 (I) and Sr2Y6.8YbEr0.2SiO26 (II). According to TEM HR microscopy and electronography, it can be seen that the nanoparticles are prone to agglomeration, have irregular shapes and amorphous character (insert) (Figures 1, 2).

According to BET, the nanoparticles sized ~23 nm (sample based on I) and ~4 nm (based on II) were found.

It is known that nanopowders together with an organic additive obtained by evaporation of solid solutions of the composition Sr2Y8–xY2Er2Yb3Si6O26 were proposed for diagnostics of pathologies in biological tissues [14].

3.1. Upconversion photoluminescence

Figure 2 shows the spectra of UCPL nanopowders produced based on Sr2La8–xY2Er2YbGeO26 (x = y = 0.075) and Sr2Y8–xY2Er2YbSiO26 (x = 0.2, y = 1).

The excitation of UCPL of Er3+ ions occurs in the presence of Yb3+ because of the absorption of the 980 nanometer laser radiation upon 2F7/2→2F5/2 transition of Yb3+ ions with the subsequent transmission of energy in Er3+ in a state 4I15/2. In addition, there is a 4I11/2→4F7/2 transition at the excitation by the second photon from a state 2F5/2 of Yb3+ ion. Besides, the excitation of the state of the 4F9/2 ion Er3+ occurs directly by two laser photons with the participation of the photons of the matrix.

Figure 1 TEMHR snapshots and electronograms (inserts) NP based on Sr6.8YbEr0.2SiO26 (a) and Sr2La7.85Er0.075Yb0.075GeO26 (b).
As is known, the primary importance of UCPL in the NIR-to-Red or NIR-to-NIR [15, 16] radiation transformations regions of the spectrum are at the excitation radiation with a wavelength of typically about 980 nm. This is particularly important for biomedical purposes. Excitation in the NIR region of the spectrum in combination with UCNP in the NIR or RED is possible due to the high transparency of biological fluids and low tissue damage.

Two intense peaks in NIR at 836 and RED at 670 nm (Figure 2a), and a very intense RED peak at ~665 nm (Figure 2b) were detected.

This luminescence can be used in photodynamic therapy (PDT) to excite a photosensitizer (PS) localized in the diseased region. Photodynamic therapy (PDT) uses special drugs called photosensitizing agents that respond to a certain wavelength of light to kill cancer cells [17]. Currently, a new generation of photosensitizers is actively developing, which have a stronger absorption in the near infrared region of the spectrum (NIR), corresponding to the optimal "transparency region" of the biotissue (700–1000 nm) [18]. High red line intensities at $\lambda_{\text{max}} = 670$ nm and near IR line at $\lambda_{\text{max}} = 836$ nm (Figure 2a) as well as $\lambda_{\text{max}} = 664$ nm (Figure 2b) indicate the nanoparticles' promise for deep tissue imaging [19].

3.2. X-ray attenuation mass coefficients

Let us consider the dependencies of mass attenuation coefficients ($\mu$) on X-ray energy for the samples Sr$_2$Y$_{0.8}$Yb$_{0.2}$Si$_6$O$_{26}$ and Sr$_2$La$_{0.75}$Er$_{0.075}$Yb$_{0.075}$Ge$_6$O$_{26}$ (Figures 3, 4).

The schedules are constructed according to the previous work [20] ($\rho$ – X-ray density). K absorption jumps of the elements Sr, Y, Yb, La are indicated. The absorption of radiation by the nanoparticles in almost the entire range of quantum energies used in X-ray diagnostics is ensured by the fact that the NP includes Sr, Y, Yb and La elements, the K absorption jumps of which lie in different parts of this range. Strontium has a K-jump at 16.10 keV, Yttrium – at 17.038 keV, Ytterbium – at 61.30 keV and Lanthanum at 39 keV. It should be noted that due to the low content of Er and Yb in the solid solutions, the K-jumps of these atoms practically do not affect the mass attenuation coefficients of the samples.

4. Conclusions

Bimodal nanoparticles were produced by PEBE in vacuum. UCPL of NPs was detected during excitation by a laser with a wavelength of 980 nm with a predominance of RED and NIR lines. Due to their optical properties, nanoparticles can be excited directly through the biotissue to visualize various pathologies. In addition, K-jumps of X-ray absorption in the energy region of 10–90 eV make it promising to use NPs as X-ray contrast agents.

Supplementary materials

No supplementary materials are available.

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