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ORIGINAL ARTICLE

SOLVOTHERMAL SYNTHESIS OF RHOMBIC SHAPE GDF$_3$:TB^{3+} NANOPARTICLES FOR BIOMEDICAL APPLICATIONS

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ABSTRACT

Purpose of the study. In this work, we have investigated the mechanism of structure formation of GdF$_3$:Tb^{3+}(15 %) nanocrystals synthesized by solvothermal synthesis in the temperature range from RT to 200 °C with a step of 50 °C.
Materials and methods. Nanocrystals of GdF$_3$:Tb^{3+}(15 %) were synthesized by the solvothermal method using a high-pressure reactor (autoclave) designed for temperatures up to 250 °C. The structure, size and morphology were determined by transmission electron microscopy (TEM), the type of crystal lattice and the size of crystallites of nanoparticles were studied by X-ray diffraction (XRD), hydrodynamic size of nanoparticles, particle size distribution, ζ-potential, agglomeration of nanoparticles in colloidal solutions were determined by dynamic light scattering (DLS), the chemical composition of the nanocrystals surface was studied by Fourier-transform infra-red spectroscopy (FT-IR), the nanoparticles ability to absorb UV radiation was analyzed by UV-visible spectroscopy (UV-vis) and X-ray excited optical luminescence (XEOL).
Results. With an increase in the temperature of the synthesis reaction, a structural change in the crystallites phase occurs from hexagonal to orthorhombic. At low temperatures, agglomerated particles consisting of hexagonal nanocrystals are formed, while at a temperature higher than the boiling point of the solvent, monodisperse rhombic-shaped nanoparticles with orthorhombic phase are formed. At mild temperatures, agglomerated particles with different morphology and with mixed hexagonal and orthorhombic phases are formed. Based on the analysis of X-ray spectrum, it was found that the size of GdF$_3$:Tb^{3+}(15 %) nanocrystals varies from 10 to 50 nm for different synthesis temperature conditions (T = RT, 50 °C, 100 °C, 150 °C, 200 °C). The hydrodynamic size of nanoparticles decreases with increasing synthesis temperature. All GdF$_3$:Tb^{3+}(15 %) nanocrystals obtained at different temperatures are transparent to visible light and absorb UV radiation. Absorption in the UV region increases with an increase in the size of particle crystallites. Upon X-ray irradiation of the colloidal GdF$_3$:Tb^{3+}(15 %) solution, X-ray excited optical luminescence spectra showed emission peaks at 490 nm, 543 nm, 585 nm and 620 nm.
Conclusion. The mechanism of structure formation of rhombic-shaped GdF$_3$:Tb^{3+}(15 %) nanocrystals has been investigated. These monodisperse rhombic-shaped nanoparticles can be used for X-ray induced photodynamic therapy (X-PDT) of superficial, solid and deep-seated tumors.

Keywords: solvothermal synthesis, GdF$_3$, Tb doped, scintillating nanoparticles, biomedical application, PDT, X-PDT

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ОРИГИНАЛЬНАЯ СТАТЬЯ

СОЛЬВОТЕРМАЛЬНЫЙ СИНТЕЗ НАНОЧАСТИЦ GDF_3:TB^{3+} РОМБИЧЕСКОЙ ФОРМЫ ДЛЯ БИОМЕДИЦИНСКИХ ПРИМЕНЕНИЙ

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РЕЗЮМЕ

Цель исследования. Исследовать механизм формирования нанокристаллов GdF_3:Tb^{3+}(15 %), полученных методом сольвотермического синтеза в интервале температур от комнатной температуры до 200 °C с шагом 50 °C.
Материалы и методы. Нанокристаллы GdF_3:Tb^{3+}(15 %) были синтезированы сольвотермальным методом с помощью реактора высокого давления (автоклав) рассчитанного на температуру до 250 °C. Структуру, размер и морфологию наночастиц исследовали методом просвечивающей электронной микроскопии (ПЭМ), тип кристаллической решетки и размер кристаллитов наночастиц определяли методом рентгеновской дифракции (РФА), гидродинамический размер наночастиц, гранулометрический состав, ζ-потенциал, агломерацию наночастиц в коллоидных растворах определяли методом динамического рассеяния света (ДРС), химический состав поверхности нанокристаллов изучали методом инфракрасной спектроскопии (ИК-спектроскопия), способность наночастиц поглощать УФ-излучение анализировали методом спектроскопии в видимой и УФ-областях спектра и рентгеновской оптической люминесценции.
Результаты. С повышением температуры реакции синтеза происходит структурное изменение фазы кристаллитов с гексагональной на орторомбическую. При низких температурах сольвотермального синтеза образуются агломерированные частицы, состоящие из гексагональных нанокристаллов, при температуре выше температуры кипения растворителя – монодисперсные наночастицы ромбической формы с орторомбической фазой. При умеренных температурах образуются агломерированные частицы различной морфологии со смешанной гексагональной и орторомбической фазами. На основании анализа рентгеновских спектров установлено, что размер нанокристаллов GdF_3:Tb^{3+}(15 %) меняется для разных температурных условий синтеза (Т = КТ, 50 °C, 100 °C, 150 °C, 200 °C) от 10 до 50 нм. Гидродинамический размер наночастиц уменьшается при увеличении температуры синтезы. Все нанокристаллы GdF_3:Tb^{3+}(15 %) полученные при разных температурах прозрачны для видимого света и поглощают УФ-излучение. Поглощение в УФ области увеличивается при увеличении размера кристаллитов частиц. Спектры оптической люминесценции с возбуждением рентгеновским излучением (XEOL) показали пики излучения в видимом диапазоне на длинах волн 490 нм, 543 нм, 585 нм и 620 нм.
Заключение. Исследован механизм формирования нанокристаллов GdF_3:Tb^{3+}(15 %) ромбической формы. Монодисперсные наночастицы GdF3: Tb3+(15 %) ромбовидной формы могут найти применение для рентгеноиндуцированной фотодинамической терапии (ФДТ) поверхностных, а также объемных и глубоколежащих опухолей.

Ключевые слова: сольвотермальный синтез, GdF_3, легированный Tb, сцинтилляционные наночастицы, биомедицинское применение, ФДТ, Рентгеновская ФДТ

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BACKGROUND

Currently, photodynamic therapy (PDT) [1] and X-ray-induced PDT are modern therapeutic methods for the treatment of superficial, as well as volumetric and deep-lying tumors [2; 3]. A key role in the therapeutic effect of PDT is played by a photosensitizer, which selectively accumulates in the tumor tissue and, when irradiated with visible or near-infrared radiation of a certain wavelength, generates the formation of reactive oxygen species (ROS), which, in turn, kill cancer cells. For the X-ray-induced PDT (R-PDT) method, it is necessary to use scintillation nanoparticles that will effectively convert X-ray radiation into visible or near-infrared light with a certain wavelength to excite a photosensitizer [4; 5].

Gadolinium (III) fluoride is a multifunctional material with effective luminescence, excellent magnetic properties and low phonon energy, high chemical and thermal stability. Gadolinium fluoride nanoparticles doped with rare earth elements (Tb, Eu, etc.) can be used as effective converters for the R-PDT method and effectively convert X-rays into visible light with a certain wavelength. The large atomic number of gadolinium makes it possible to effectively absorb X-rays, so gadolinium fluoride nanoparticles can be used as a contrast agent for CT imaging. In addition, GdF_3 nanoparticles can be used in MRI due to their paramagnetic properties. When irradiated with both UV radiation and X-rays, GdF_3 nanoparticles doped with Tb^{3+} have strong green emission with a maximum at 545 nm and less intense satellite peaks at ~490, 585 and 620 nm due to electronic transitions from the excited state of $^5D_4$ to ^7F_J (J = 6–3) of the ground states of the Tb^{3+} ion [6].

Gadolinium trifluoride nanoparticles were obtained by several synthesis methods, including co-deposition [7], hydrothermal synthesis [6], solvothermal synthesis [8], microwave synthesis [10]. For example, Zhang et al. synthesized GdF_3:Eu^{3+} nanoluminophores with a hexagonal or orthorhombic structure at room temperature using the chemical co-deposition method [7]. The structure and morphology of GdF_3:Eu^{3+} nanoluminophores were controlled using various fluorine precursors. Hexagonal GdF_3:Eu^{3+} nanocrystals were formed using $NaBF_4$ as a fluoride precursor, whereas orthorhombic GdF_3:Eu^{3+} nanocrystals were obtained using a NaF or NH4F fluoride precursor. It has also been experimentally established that hexagonal GdF_3:Eu^{3+} nanoluminophores emit significantly stronger Eu3+ luminescence than orthorhombic ones. Samantha et al. A simple microwave method was reported for the synthesis of stable Eu^{3+}-doped GdF_3 nanocrystals with a hexagonal phase functionalized with polyvinylpyrrolidone at higher temperatures (up to 220 °C), achieved by adjusting the viscosity of solvents, as well as using KF as a source of fluorine [8]. Both the morphology and the size of GdF_3 nanocrystals can also be varied by adjusting the reaction conditions. Wang et al. various monodisperse colloidal nanocrystals GdF3: Yb, Er with increased frequency with different shapes, sizes and alloying impurities were synthesized using microwave synthesis [10]. In addition to highly monodisperse spherical particles, they prepared monodisperse slices of rhombic shape, showing a tendency to self-assemble into stacks. Sui et al. [9] reported the behavior of the orthorhombic REF_3 phase at high pressure (RE = Sm to Lu and Y). Pressure-induced GdF_3 phase transitions were studied at room temperature. It is established that the pressure range of the phase transition from the orthorhombic to the hexagonal phase is 5.5–9.3 GPa for GdF3.

In this paper, the mechanism of formation of GdF_3:Tb^{3+}(15 %) nanocrystals synthesized by solvothermic synthesis in the temperature range from room temperature to 200 °C. The physicochemical properties were studied by transmission electron microscopy (TEM), X-ray diffraction (XRD), dynamic light scattering (DRS), infrared spectroscopy, spectroscopy in the visible and UV spectral regions and X-ray optical luminescence.

MATERIALS AND METHODS

Gadolinium nitrate hexahydrate Gd $(NO_3)_3{\cdot}6H_2O$ (99.9 %) and terbium chloride hexahydrate $TbCl_3{\cdot}6H_2O$ (99.9 %), ammonium fluoride NH_4F (98 %) were purchased from Alfa Aesar (Haverhill, Massachusetts, USA). Ethylene glycol was purchased from Sigma-Aldrich (Burlington, Massachusetts, USA). All chemicals were used without additional purification.

The physicochemical characteristics of GdF_3:Tb^{3+}(15 %) nanocrystals (T = RT, 50 °C, 100 °C, 150 °C, 200 °C) were determined by the following experimental methods. The size, shape and morphology were studied using TEM on a Tecnai G2 Spirit BioTWIN device (FEI, USA). The type of crystal lattice and the average size of nanoparticle crystallites were determined by XRD on a D2 PHASER diffractometer (Bruker Corp., Germany). The hydrodynamic size of nanoparticles, granulometric composition, ζ-potential, and agglomeration of nanoparticles in colloidal solutions were determined by DRS on a NANO-Flex particle size analyzer (MicroTrac GmbH, Germany) and STABINO (ParticleMetrix, USA). The quantitative and qualitative chemical composition and concentration of alloying elements were evaluated using a two-dimensional microrentgenofluorescence (XFA) spectrometer M4 Tornado (Bruker Corp., Germany). The surface chemistry was studied using infrared Fourier spectroscopy (FTIR) on a Vertex 70 spectrometer (Bruker Corp., Germany). Emission spectra (XEOL) of nanomaterial powders and colloidal aqueous solutions were studied using a RAP-90U X-ray tube with a protective casing and a Shimadzu UV-2600 dual-beam spectrophotometer (Shimadzu, Japan).

GdF_3:Tb^{3+} nanocrystals synthesis

GdF_3:Tb^{3+} nanocrystals (15 %) were obtained by the solvothermal synthesis method. To obtain 160–200 mg of GdF_3:Tb^{3+} nanocrystal powder (15 %), it is necessary to: dissolve 0.85 mmol Gd $(NO_3)_3H_2O$ (*m* = 0.384 g) and 0.15 mmol TbCl3·C2·6H2O (*m* = 0.056 g) in 10 ml of ethylene glycol (EG) in a beaker at room temperature. For better dissolution of chemical reagents, ultrasonic dispersants can be used. After mechanical stirring for about 1 hour, add 3 mmol NH4F (*m* = 0.1111 g), previously dissolved in 10 ml of ethylene glycol (EG), drop by drop. During the reaction, the previously transparent solution becomes cloudy and white due to the deposition of doped gadolinium fluoride. Further, the resulting solution was subjected to heat treatment in a Teflon autoclave in the temperature range from RT to 200 °C with intensive stirring for 24 hours. The final product was washed three times with distilled water using centrifugation. After the last centrifugation, the white nanocrystals were dried in a drying cabinet at 60 °C. The obtained nanocrystals were denoted respectively GdF_3 GdF_3:Tb^{3+} (15 %) (T = RT, 50 °C, 100 °C, 150 °C, 200 °C). Colloidal aqueous solutions of GdF_3:Tb^{3+} nanocrystals were prepared by dispersing nanocrystals in bidistilled water using an ultrasonic disperser.

RESEARCH RESULTS AND DISCUSSION

We have studied the mechanism of formation of GdF_3:Tb^{3+} (15 %) nanocrystals (T = RT, 50 °C, 100 °C, 150 °C, 200 °C) obtained by the solvothermal synthesis method in the temperature range fromRT to 200 °C in increments of 50 °C. The solvothermal method is a chemical reaction occurring in a solvent at a temperature above the boiling point of the solvent (usually < 250 °C) in a sealed reactor. Ethylene glycol with a boiling point of 197 °C was used as a solvent. By varying the synthesis parameters: temperature and reaction time, this method makes it possible to obtain nanocrystals with size control, morphology and a high level of crystallinity.

Figure 1a shows diffractograms in the range of 22°–32° degrees of nanocrystals obtained during synthesis at various reaction temperatures (T = RT, 50 °C, 100 °C, 150 °C, 200 °C) for 24 hours. It is established that with an increase in the temperature of the synthesis reaction, the structure of nanocrystals undergoes a structural change from the hexagonal to the orthorhombic phase. At a synthesis temperature of 50 °C, a purely hexagonal structure is observed, and at a temperature of 200 °C a pure orthorhombic structure with no secondary phases is already observed. At moderate temperatures, a mixed phase of hexagonal and orthorhombic phases is observed. Figure 1b shows diffractograms of nanocrystals of hexagonal and orthorhombic phases. The position of the peaks and their intensity correspond exactly to the diffractograms of orthorhombic GdF_3 (ICSD chart 00-012-0788) and hexagonal SmF3 (ICDS chart PDF No. 01-072-01439). No additional peaks of any secondary phases were detected.

Based on the Scherrer equation, reflex broadening was used to estimate the average size of crystallites. The average size of crystallites in GdF_3:Tb^{3+} nanocrystals (15 %) varies from 10 nm to 50 nm for different synthesis reaction temperatures: from room temperature (RT), 50 °C, 100 °C, 150 °C, 200 °C. X-ray fluorescence analysis (XFA) confirmed the chemical composition of Tb/Gd (15 %) for all synthesized nanocrystals, which indicates good solubility of rare earth element salts in the process of solvothermal synthesis. According to the data of dynamic light scattering in colloidal solutions of nanocrystals, the hydrodynamic radius of nanoparticles gradually decreases from 220 ± 200 nm for RT, 174 ± 90 nm

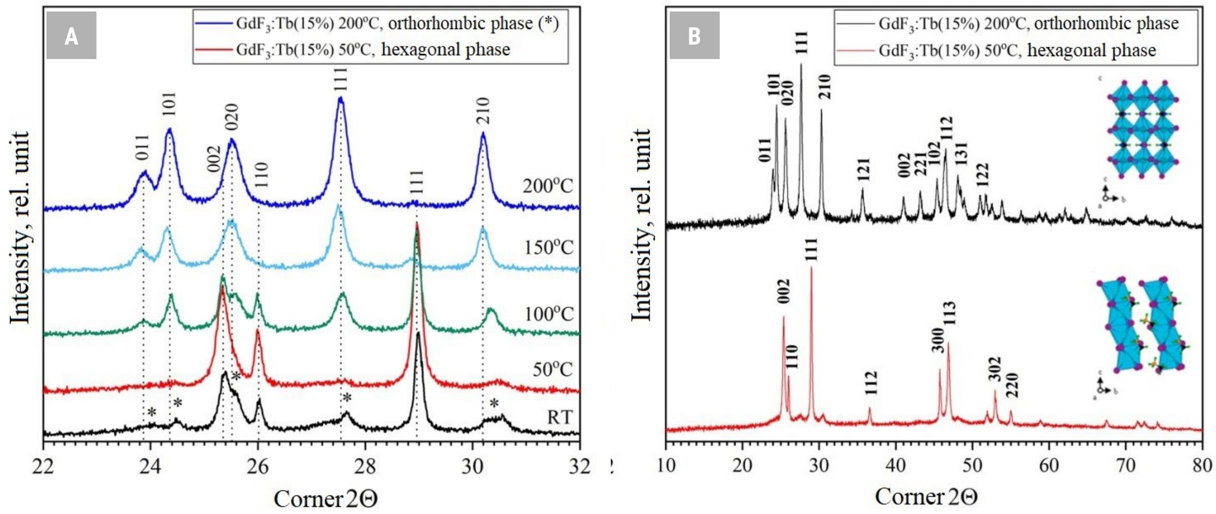

Fig. 1. a) GdF_3:Tb^{3+} diffractograms of nanocrystals (15 %) (T = RT, 50 °C, 100 °C, 150 °C, 200 °C); b) GdF_3:Tb^{3+} diffractograms (15 %) (T = 50 °C) of hexagonal phase and GdF_3:Tb^{3+} (15 %) (T = 200 °C) orthorhombic phase.

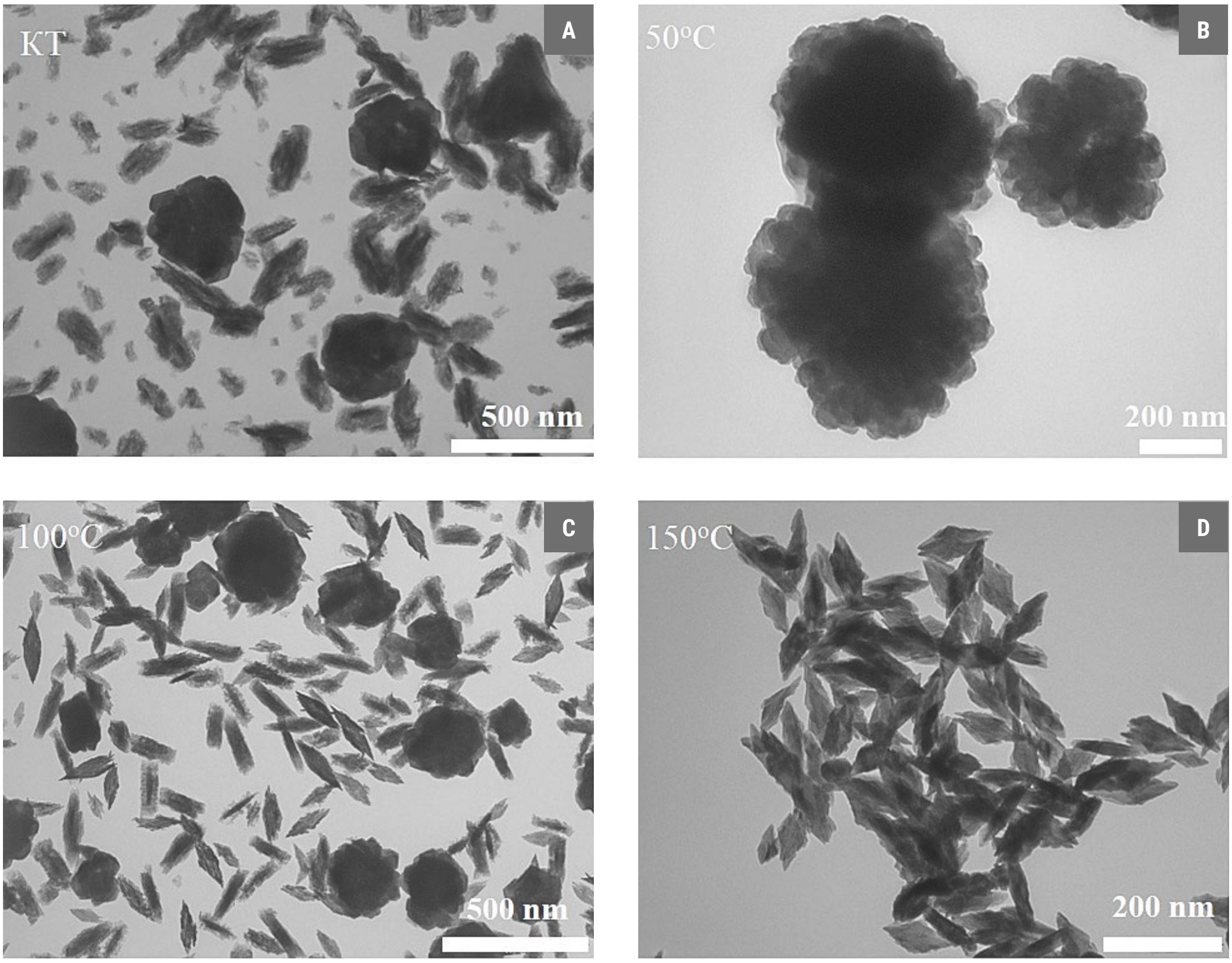

Fig. 2. a) GdF_3:Tb^{3+} nanocrystals TEM-imaging (15 %) (RT); b) hexagonal phase GdF_3:Tb^{3+} nanocrystals TEM-imaging (15 %) (50°C); c) GdF_3:Tb^{3+} nanocrystals TEM-imaging (15 %) (100°C); d) GdF_3:Tb^{3+} rhombic shape with orthorhombic phase nanocrystals TEM-imaging (15 %) (150°C).

for 50 °C, 150 ± 116 nm for 100 °C, 57 ± 39 nm for 150 °C, to 48 ± 32 nm for 200 °C. The decrease in the hydrodynamic radius is associated with the recrystallization of nanocrystallites during heat treatment during synthesis and the reduction of the interparticle space in agglomerated particles.

Figure 2 shows TEM images of nanocrystals obtained at various synthesis temperatures (RT 50 °C, 100 °C, 150 °C). Figure 2a shows agglomerated particles of various morphologies synthesized at room temperature (RT) with an average size of 150–180 nm, consisting of small orthorhombic phase nanoparticles up to 10 nm in size. There are also large agglomerated particles consisting of hexagonal particles up to 50 nm in size, with well-defined faces and good crystallinity. Figure 2b shows large agglomerated particles up to 500 nm in size in the form of "flowers" consisting of hexagonal phase crystallites. The crystallites have a hexagonal shape and a size of 30–50 nm. Figure 2b shows agglomerated nanoparticles obtained at a reaction temperature of 100 °C in the form of "flowers" and rhombic and spindle-shaped particles. In these types of agglomerated nanoparticles, regions with higher and lower densities are noticeable. A higher temperature is required for the formation of rhombic nanoparticles with good crystallinity. The image also contains agglomerated nanoparticles up to 200 nm in size, rectangular and spindle-shaped, consisting of small crystallites up to 10 nm in size. Figure 2g shows nanoparticles

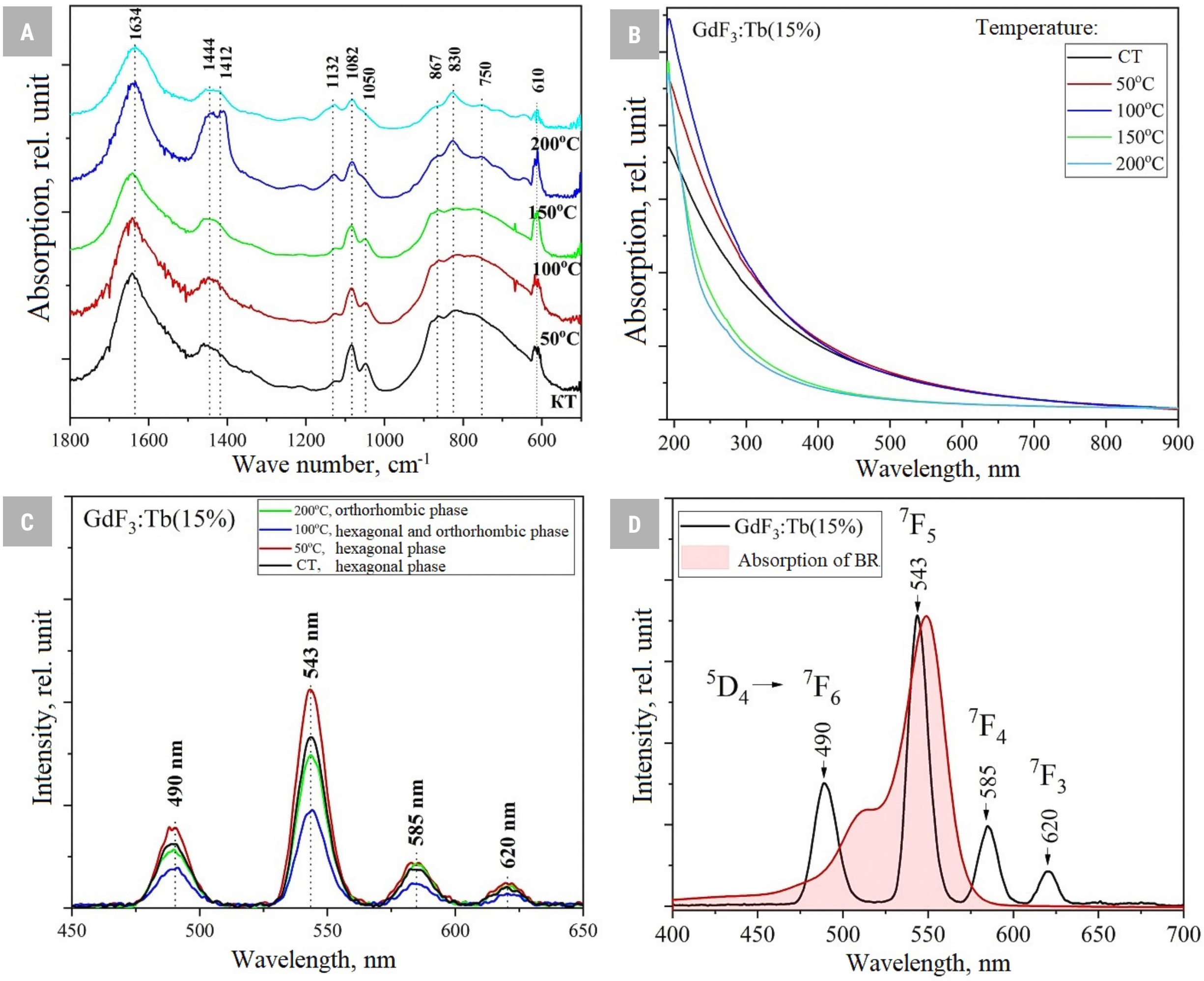

Fig. 3. Absorption spectrum in a) IR range; b) in visible and UV regions; c) optical luminescence spectrum with XEOL of GdF_3:Tb^{3+} (15 %) nanocrystals (T = RT, 50°C, 100°C, 150°C, 200°C); d) comparison of the spectrum of XEOL nanoparticles PEG@GdF_3:Tb^{3+}(15 %) excited by X-ray irradiation (35 kV, 16 mA), and the absorption spectrum of the UV-visible photosensitizer bengal pink (BP).

obtained at a reaction temperature of 200 °C in the form of rhombic nanoparticles.

Figure 3a shows the absorption spectra in the IR range of GdF_3:Tb^{3+} nanocrystals (15 %) (T = RT 50 °C, 100 °C, 150 °C, 200 °C). Wide peaks in the region of 1600–1650 cm^{-1} and 650–950 cm^{-1} are associated with bending and vibrational modes of adsorbed water molecules on the surface of nanocrystals [5]. The valence and deformation vibrations C = O are at 1665 and 1436 cm^{-1}. The band at 610 cm^{-1} can be attributed to vibrations of the gadolinium fluoride lattice, which confirms the formation of gadolinium fluoride nanocrystals. Peaks ~1412 and 1444 cm^{-1} refer to methylene scissor and valence vibrations of C-O-C EG. UV-visible spectra of GdF_3:Tb^{3+} nanocrystals (15 %) (T = RT, 50 °C, 100 °C, 150 °C, 200 °C) are shown in Figure 3b. All the obtained nanocrystals are transparent to visible light and absorb UV radiation. The absorption in the UV region increases with the increase in the size of the crystallites of the particles. Figure 3b shows optical luminescence spectra with XEOL of GdF_3:Tb^{3+} nanocrystals (15 %) (T = RT, 50 °C, 100 °C, 150 °C, 200 °C). Fluorescence emission can be excited by both UV light and X-ray radiation, which gives the same typical Tb^{3+} emission profile. Strong green glow of scintillation nanocomposites PEG@GdF_3:Tb^{3+} (15 %) with a main peak at 545 nm and three satellite peaks at 490, 585 and 620 nm is due to electronic transitions from the excited state of 5D4 to the ground states of Tb^{3+} ^7F_J ions (J = 6–3). Figure 3g shows a comparison of the spectrum of XEOL nanoparticles PEG@GdF_3:Tb^{3+} (15 %) excited by X-ray radiation (35 kV, 16 mA), and the absorption spectrum of the bengal pink photosensitizer (BP).

CONCLUSION

In this paper, the mechanism of formation of GdF_3:Tb^{3+} (15 %) nanocrystals obtained by solvothermal synthesis in the temperature range from RT to 200 °C. At low temperatures, agglomerated particles consisting of hexagonal nanocrystals are formed, and at temperatures above the boiling point of the solvent, monodisperse rhombic nanocrystals with an orthorhombic phase are formed. At moderate temperatures, agglomerated particles of various morphologies with mixed hexagonal and orthorhombic phases are formed. Under X-ray irradiation of a GdF_3:Tb^{3+} (15 %) colloidal solution, optical luminescence spectra with XEOL showed radiation peaks at 490 nm, 543 nm, 585 nm and 620 nm. Monodisperse nanocrystals of rhombic shape can be used for X-ray induced photodynamic therapy (X-PDT) of surface, volume and deep-lying tumors.

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