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Composite materials based on nanoporous SiO_2-matrices and TiO_2 nanoparticles

***O.N.Bezkrovnaya*[1], *I.M.Pritula*[1], *O.M.Vovk*[1], *Yu.A.Gurkalenko*[2], *A.N.Shaposhnik*[3], *D.S.Sofronov*[3], *Y.V.Taranets*[1]**

[1]Institute for Single Crystals, STC "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Nauky Ave., 61001 Kharkiv, Ukraine
[2]Institute for Scintillation Materials, SSI "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Nauky Ave., 61001 Kharkiv, Ukraine
[3]Division of Functional Materials Chemistry, STC "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Nauky Ave., 61001 Kharkiv, Ukraine

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SiO_2:TiO_2 composites were obtained by saturation of SiO_2-matrices (with a porosity of ~ 30 % and ~ 42 %) with a suspension of TiO_2 nanoparticles and subsequent annealing to 700°C. It was shown that, due to annealing of the composites in the temperature range of 400–700°C, there was observed agglomeration of TiO_2 nanoparticles in the pores of the SiO_2-matrices, that manifested itself in an increase of the absorption in wavelength range of 390–800 nm. The presence of diffraction rings in the electron microdiffraction images confirms formation of TiO_2 crystallites in SiO_2:TiO_2 composites. The content of titanium in the composite less than 1 % relative to silicon did not allow to reveal crystalline TiO_2 phase in the composites by powder X-ray diffraction method. TiO_2 is probably present in the composites based on SiO_2-matrices with high porosity both in the form of crystallites and in amorphous state.

Keywords: SiO_2-matrices, TiO_2 nanoparticles, composites, absorption.

Композитні матеріали на основі нанопористих SiO_2-матриць і наночастинок TiO_2. *О.М.Безкровна, І.М.Притула, О.М.Вовк, Ю.О.Гуркаленко, А.М.Шапошнік, Д.С.Софронов, Ю.В.Таранець*

Отримано композити SiO_2:TiO_2 шляхом насичення SiO_2-матриць (з пористістю ~ 30 % і ~ 42 %) суспензією наночастинок TiO_2 і подальшим відпалом до температури 700°C. Показано, що у результаті відпалу композитів в інтервалі температур 400–700°C спостерігається агломерація наночастинок TiO_2 у порах SiO_2-матриці, що проявляється в збільшенні поглинання в інтервалі довжин хвиль 390–800 нм. Утворення кристалітів TiO_2 у композитах SiO_2:TiO_2 підтверджує наявність дифракційних кілець на знімках електронної мікродифракції. Вміст в композиті титану по відношенню до кремнію менше ніж 1 % не дозволило виявити кристалічну фазу TiO_2 у композитах методом порошкової рентгенівської дифракції. Ймовірно, TiO_2 у композитах на основі високопористих SiO_2-матриць присутній як у вигляді кристалітів, так і в аморфному стані.

Получены композиты SiO_2:TiO_2 путем насыщения SiO_2-матриц (с пористостью ~ 30 % и ~ 42 %) суспензией наночастиц TiO_2 и последующим отжигом до температуры 700°C. Показано, что в результате отжига композитов в интервале температур 400–700°C наблюдается агломерация наночастиц TiO_2 в порах SiO_2-матрицы, что проявляется в увеличе-

нии поглощения в интервале длин волн 390–800 нм. Образование кристаллитов TiO_2 в композитах SiO_2:TiO_2 подтверждает наличие дифракционных колец на снимках электронной микродифракции. Содержание в композите титана по отношению к кремнию менее 1 % не позволяло обнаружить кристаллическую фазу TiO_2 в композитах методом порошковой рентгеновской дифракции. Вероятно, TiO_2 в композитах на основе высокопористых SiO_2-матриц присутствует как в виде кристаллитов, так и в аморфном состоянии.

1. Introduction

Organo-inorganic sol-gel hybrid compounds attract attention of researchers due to their ability to combine the functional properties of organic and inorganic constituents, uniformly distributed into a bulk of the samples, in one material. Today sol-gel synthesis is one of most diverse and promising methods of "soft" chemistry for creation of nanostructured oxides that can be effectively used in the field of photonics and photocatalysis [1]. An increased interest in nanoporous structures based on SiO_2 synthesized by sol-gel method [2, 3] is due to the optical quality of these materials, and to a significant expansion of the field of their use for creation of new optoelectronic devices. SiO_2-matrices are highly transparent in Vis-NIR spectral range, and possess high mechanical and radiation resistance combined with high absorption capacity and chemical stability [2].

In a number of papers there is considered preparation of nanoporous silicate matrices with nanoparticles distributed in a macrovolume, including PbS nanocrystals with a diameter of 5–15 nm, for creation of narrow-band-gap semiconductors [4]. As shown in [5, 6], incorporation of metal oxide nanoparticles, in particular, titanium dioxide (TiO_2) nanocrystals with a high cubic susceptibility ($\chi^{(3)}$), into a dielectric matrix, increases the nonlinear optical (NLO) response of the matrix due to appearance of additional charge carriers. Such materials may find practical application in ultrafast optical switches and laser limiters [5, 6]. On the other hand, due to the presence of anion-exchange properties, for example, in highly porous silica-titanium matrices, they may effectively encapsulate dyes sensitive to pH, for creation of sensors to be used in determination of acidity of media. In particular, the obtaining of encapsulated indicator sol-gel silica-titania nanocomposite matrices was reported in [7]. In [8] there was considered creation and application of mesoporous SiO_2–TiO_2 hybrid nanoparticles and thin films based on them as optical pH sensing and optochemical sensors. Nanoporous composites with high transparency in the visible range of the spectrum can be used as photoactive media. For instance, in [9] amorphous TiO_2 with long-range atomic disorder was shown to play an important role in photocatalytic performances and be used as a base for fabrication of novel amorphous nanomaterials for photochemical applications.

Nanostructured materials made from titanium dioxide (TiO_2) are attractive for application in the fields of photocatalytic degradation of pollutants, photoreduction of carbon dioxide, and photocatalytic organic synthesis. As shown in [9], some physicochemical properties of TiO_2, such as light absorption, surface adsorption, separation of charge carriers, photocatalytic reactivity, etc. may be defined by disordered arrangement of its atoms. Amorphous materials have the typical structure of atomic disorder over long distances, and are isotropic both physically and chemically. Due to these properties they exhibit high activity in photocatalysis caused by efficient absorption of light and high specific surface area. The latter to a considerable extent defines the fact that amorphous TiO_2 can play an important role in improvement of the photocatalytic activity of the material. TiO_2 nanoparticles and clusters (synthesized from titanium tetra-iso-propoxide precursor) have an increased chemical activity [10, 11]. Moreover, they can be easily applied in the form of monolayer nanocoatings on substrates, as well as be incorporated into porous matrices.

The aim of this work was to synthesize SiO_2-matrices with variable density and porosity, to obtain SiO_2:TiO_2 composites on their base by incorporating TiO_2 nanoparticles into nanoporous SiO_2-matrices with subsequent annealing SiO_2:TiO_2 to high temperatures, to study the structure as well as the spectral and luminescent properties of these composites.

2. Experimental

SiO_2-matrices were synthesized using the sol-gel method by hydrolysis of tetraethoxysilane (TEOS; Aldrich) with the addition of nitric and hydrofluoric acids

(HF), ethanol and distilled water as described in [3, 12]. The solid xerogels were shaped as parallelepipeds with the dimensions ~ 0.45×0.45×1.5 cm^3. The samples of pure SiO_2-matrices were annealed in air at temperatures up to 700°C, the rate of temperature rise was 100°C/hr and then 150°C/hr. The porosity of the matrices was estimated by the hydrostatic weighing method as in [12, 13].

Synthesis of amorphous titanium-oxo-alkoxo nanoparticles was carried out by the sol-gel method in a special reactor for preparation of nanostructured TiO_2 with turbulent fast micromixing [10, 14]. Titanium (IV) isopropoxide)/propan-2-ol (Alrich) and the mixture of H_2O/propan-2-ol were used as precursors, isopropanol being the solvent. The temperature of the reaction mixture was maintained to an accuracy of 0.1°C. As a result, there were obtained TiO_2 clusters and TiO_2 nanoparticles with a size of 2–5 nm which remained stable during the period from three hours to a day. The size of the nanoparticles was controlled using a fiber-optical probe by the method of dynamical scattering of He–Ne laser radiation. SiO_2:TiO_2 composites were prepared by saturation of SiO_2-matrices (annealed to 700°C) with TiO_2 nanoparticles in isopropanol. Then the composites were dried at 60°C and annealed at temperatures up to 400°C, 550°C and 700°C in air. After that SiO_2:TiO_2 composites were annealed at 700°C during 4 hours. Two types of SiO_2-matrices were used for saturation by TiO_2 nanoparticles: the ones with a porosity of ~ 30 % (type SiO_2-matrice (A)) and ~ 42 % (type SiO_2-matrice (B)). The porosity was regulated by the addition of HF acid in the synthesis of pure SiO_2-matrices. Accordingly, after saturation, there were obtained SiO_2:TiO_2(A) and the SiO_2:TiO_2(B) composites.

The absorption spectra of the samples were measured by means of a Lambda 35 UV/Vis Spectrophotometer (Perkin-Elmer, USA) in 200–1100 nm region. The luminescence spectra were obtained using a fluorimeter FluoroMax-4 (Horiba Jobin Yuon, USA). The infrared spectra of the crystals and of the powders were recorded using Spectrum One PerkinElmer at room temperature in 400–4000 cm^{-1} region with a resolution of 1 cm^{-1} by the KBr pellet technique. The structure of SiO_2 xerogel was checked using a transmission electron microscope (TEM) (EM-125, SELMI, Ukraine) with an accelerating voltage of 100 kV. The samples for TEM investigation were prepared by the following procedure: the samples of the composites were ground between two glass plates with subsequent deposition on a carbon film without preliminary sonication (SiO_2:TiO_2(A)) or after sonication during 30 sec in isopropyl alcohol (SiO_2:TiO_2 (B)).

The crystalline structures of pure SiO_2-matrice, SiO_2:TiO_2 composites annealed at temperatures up to 580°C, SiO_2:TiO_2 powder and quartz glass were investigated by a X-ray three-crystal diffractometer (TCD) in CuK_α-radiation (λ = 1.54051 Å) as in [15]. The phase composition of the synthesized SiO_2:TiO_2 sample (annealed during 4 hours at 700°C) was established by the method of X-ray phase analysis. For X-ray analysis there was used a Siemens D500 powder diffractometer (CuK_α radiation, graphite monochromator, Bragg-Brentano geometry).

All the studies were performed at room temperature.

3. Results and discussions

There were synthesized pure SiO_2-matrces meant for their subsequent saturation with TiO_2 nanoparticles for the making of SiO_2:TiO_2 composites. It is known that HF acid used as a catalyst for the sol-gel process allows to synthesize SiO_2-matrices with a controlled porosity [3, 16]. Earlier , we obtained SiO_2-matrices with an open porosity from 32 % to 75 % [12] and used them for saturation with organic molecules [12, 13].

It should be noted that the structure of SiO_2-matrices saturation with a solution of nanoparticles is a branched system of SiO_2 chains which form interconnected pores. At the same time, the samples of SiO_2-matrices should not be destroyed during their saturation with active additives. As shown in our paper [12], at the formation of the samples with a porosity less than 30 % and high density there arise additional stresses in the xerogel structure due to the appearance of a large number of small pores. Such SiO_2-matrices can be mechanically destroyed as a result of annealing, or upon saturation with the solutions, and introduction of the solution containing TiO_2 nanoparticles into the bulk of such SiO_2-matrices may be difficult. SiO_2-matrices had pores with a size of 600 nm and more when their porosity increased above 55 % [12]. That may lead to the formation of cracks in the samples when they are saturated by the solution of TiO_2 nanoparticles, as well as during drying and

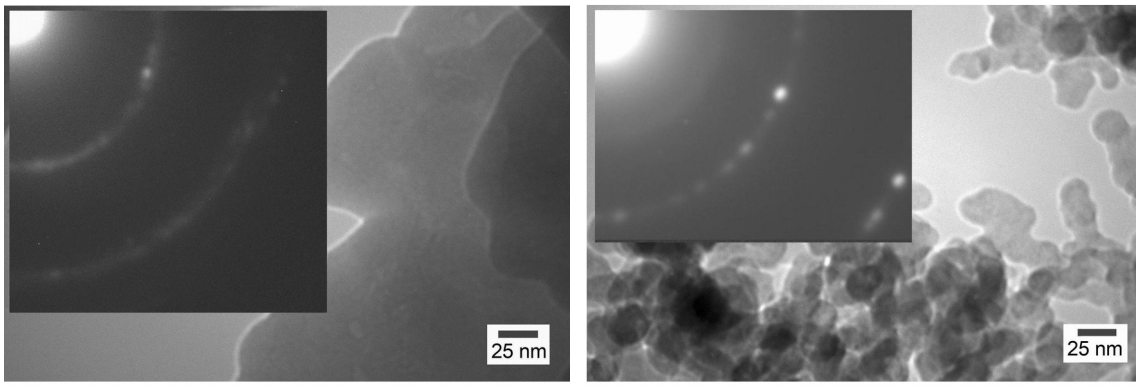

Fig. 1. TEM images of SiO_2:TiO_2 (A) (a) and SiO_2:TiO_2 (B) (b) composites annealed at a temperature up to 580°C.

annealing of the composites. Based on these factors, the matrices with an open porosity of 30–55 % were selected for the obtaining of SiO_2:TiO_2 composite materials. The mass ratio of Ti:Si in the SiO_2:TiO_2(B) composite determined by atomic emission spectrometry was found to be $8 \cdot 10^{-3}$ wt. %.

The morphology of SiO_2:TiO_2 composites was investigated using TEM (Fig. 1a–c). We have previously shown [12] that the structure of pure SiO_2-matrices is formed by chains of 6–12 nm nanoparticles and small (5–12 nm) pores. There are also large pores with a size of 100–200 nm and more, which facilitate penetration of the solvent and TiO_2 nanoparticles deep into the saturated SiO_2-matrices. As follows from Fig. 1a, the pores are not observed in the structure of SiO_2:TiO_2(A) composite. This is probably due to the filling of the pores with TiO_2 nanoparticles. At the same time, the TEM image of the sample of SiO_2:TiO_2(B) subjected to ultrasonic treatment testifies to the presence of agglomerates with a size up to 29 nm which consist of smaller particles, and of the ones with a size up to 50 nm (Fig. 1b).

Using the methods of microdiffraction and X-ray structural analysis there were performed structural studies of the obtained composites (Fig. 1, Fig. 2). The presence of diffraction rings in the images of SiO_2:TiO_2 (A) and SiO_2:TiO_2(B) composites measured using TEM points to possible formation of TiO_2 crystallite phase (Fig. 1a,b). The curves of coherent scattering regions (CSR) of bulk samples of pure SiO_2 matrices, SiO_2:TiO_2(B) composite, ground SiO_2:TiO_2(B) composite, and quartz glass are shown in the diffractograms (Fig. 2a) measured on a three-crystal diffractometer. All the curves are characterized by the presence of a wide halo in the region of 22–23° with small CSR. This confirms amorphous structure of the studied samples, and is apparently due to amorphous structure of SiO_2-matrice itself [17]. An additional peak with larger CSRs for pure SiO_2-matrice (curve *1*) and SiO_2:TiO_2(B) composite (curve *2*) testifies to the presence of a bulk sample texture associated with peculiarities of xerogel formation. The surface texture was not analyzed due to the fact that the penetration depth of X-rays varied from hundredths to tenths of a millimeter, depending on the density of the material and radiation, thereat the size of the unit cell is usually much smaller (of the order of several angstroms or tens of angstroms).

According to the results of studying the samples of SiO_2:TiO_2(A) and SiO_2:TiO_2(B) composites (annealed at 700°C for 4 h) by powder diffraction, we can say that the phase TiO_2 in the crystalline form is not observed in the samples (Fig. 2b). This is possibly due to the fact that the used method does not allow to reveal the presence of TiO_2 nanocrystals at their low concentration in SiO_2-matrice (as mensioned above, Ti concentration with respect to Si does not exceed 1 %).

To estimate the effect of TiO_2 nanoparticles on the surface state of the xerogel, there were measured IR spectra of SiO_2-matrices with different porosities before their saturation with TiO_2 nanoparticles, and those of the finished samples (Fig. 3). The IR spectra of the samples have absorption bands with maxima at 810–801 cm^{-1}; a broad absorption band in the region of 1080–1240 cm^{-1} with a maximum at 1100–1080 cm^{-1}; shoulder-shaped absorption

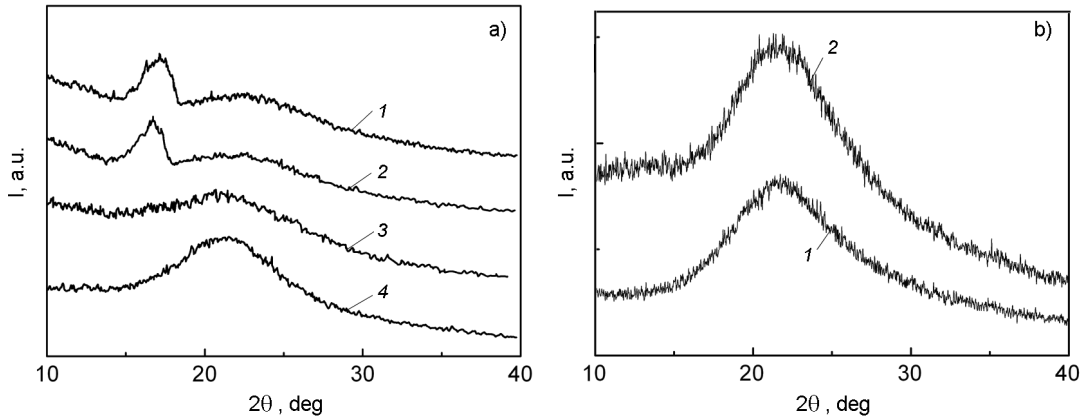

Fig. 2. Diffractograms of: pure SiO_2 matrix (*1*), SiO_2:TiO_2 (B) composite annealed at a temperature up to 580°C (*2*), SiO_2:TiO_2(B) powder from this composite (*3*), quartz glass (*4*) (a); and of SiO_2:TiO_2 (A) (*1*) and SiO_2:TiO_2(B) (*2*) composites annealed during four hours at 700°C (b).

bands with maxima at 1240 cm^{-1} and 960–964 cm^{-1}; and a band in the region of 1750–1640 cm^{-1}. It should be noted that the bands with wavenumbers from 1080 cm^{-1} to 1200 cm^{-1} correspond to Si–O(–Si) vibrations, the band in the 960 cm^{-1} region is bound up with Si–O(H) stretching vibrations, while the peak at ~ 1100 cm^{-1} is due to Si–O(–Si) stretching vibrations of a more linear structure of the xerogel [18]. The shift of the frequencies of stretching vibrations of Si–O–Si towards higher wavenumber values (higher frequencies) is correlated to strengthening of the network in the matrices [19]. The presence of the absorption peak in the region of 1060 cm^{-1} for sol-gel TiO–SiO films, also observed in [20], may be attributed to asymmetric vibration of Si–O–Si bonds. In [21] the appearance of the peaks at 793 cm^{-1} and 1110 cm^{-1} was explained by symmetric and asymmetric Si–O–Si stretching vibration, respectively.

The position of the band bound up with Si–O(–Si) vibrations for pure SiO_2-matrices of type (A) and SiO_2:TiO_2(A) composite corresponds to the region of 1083 cm^{-1} (Fig. 3, spectra 1 and 3). For pure SiO_2-matrices of type (B) and SiO_2:TiO_2(B) composite it is in the region of 1096 cm^{-1} (Fig. 3, spectra 2 and 4) (Fig. 3, spectra 2 and 4). The initial SiO_2-matrices had different porosities: ~ 30 % for type (A) and ~ 42 % for type (B). For the synthesis of the former there was used a smaller amount of HF acid. The observed shift of the peak towards higher wavenumbers in the case of a higher HF concentration is in good agreement with our earlier investigation [12]. Note that in [12]

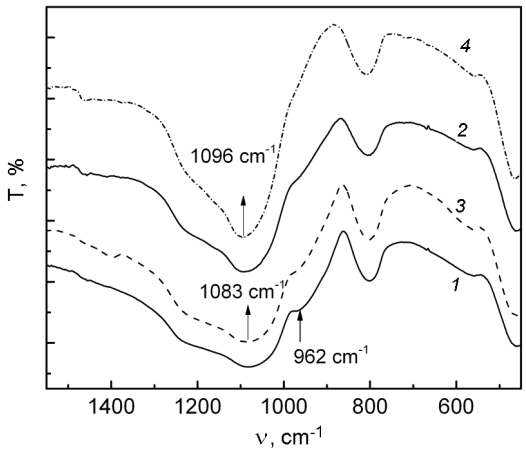

Fig. 3. FTIR-spectra of: pure SiO_2-matrix of type (A) (*1*), pure SiO_2-matrix of type (B) (*2*), SiO_2:TiO_2(A) composite (*3*), SiO_2:TiO_2(B) composite (*4*). Pure SiO_2-matrix and SiO_2:TiO_2 composites were annealed at a temperature up to 700°C.

we reported a shift in the position of the peaks towards higher wavenumbers from 1089 cm^{-1} to 1104 cm^{-1} with an increase in HF concentration used in the synthesis of the matrices (when the porosity of matrices changed from 30 to 75 %).

Weakening of the absorption band intensity in the region of 960–964 cm^{-1} (bound up with vibrations of Si–O(H) bonds [18]) in comparison with the intensity of the absorption bands of pure SiO_2-matrice of the type (A) (Fig. 3, spectra, 2) is clearly seen in the IR spectrum of SiO_2:TiO_2(A) composite (Fig. 3, spectra 3). At the same time, the absorption band in the region of 960–964 cm^{-1} is not observed in the IR spectrum of SiO_2:TiO_2(B) composite (Fig. 3, spectrum 4). Such a

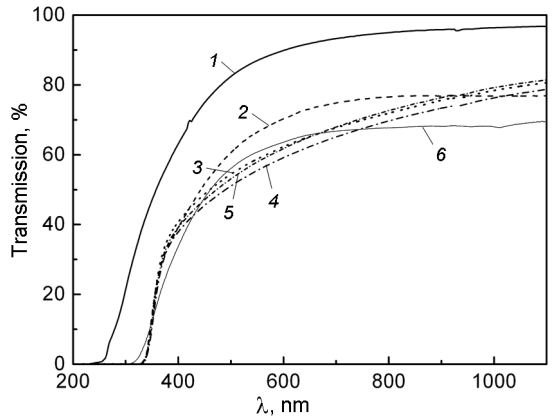

Fig. 4. Transmission spectra of pure SiO_2-matrix of type (B) without TiO_2 (*1*), SiO_2:TiO_2 (A) composite annealed at 580°C (*6*), and SiO_2:TiO_2(B) composite, annealed at temperatures of 60°C (*2*), 400°C (*3*), 580°C (*4*), 700°C (*5*). All pure SiO_2-matrices before saturation of TiO_2 were previously annealed at a temperature up to 700°C.

change in the spectrum is probably due to the interaction of OH groups on the silica surface with TiO_2 nanoparticles.

As seen from Fig. 4, pure SiO_2-matrix is highly transparent in the wavelength range of 500–800 nm. Its spectral transmission is 90 % at 600 nm and 95 % at 800 nm. The transmission of pure SiO_2-matrice after its saturation with TiO_2 nanoparticles decreases to 64 % and 68 % for SiO_2:TiO_2(A) composite (Fig. 4, spectrum 6) and to 70 % and 76 % for SiO_2:TiO_2(B) composite (Fig. 4, spectrum 2) for the wavelengths of 600 nm and 800 nm, respectively. Upon further annealing of SiO_2:TiO_2(B) composite in the temperature range of 400–700°C, the transmission of the sample decreases to 62–58 % at 600 nm and to 72–70 % at 800 nm (Fig. 4, spectra 3–5).

The absorption spectra of pure SiO_2-matrices and SiO_2:TiO_2(B) composite annealed in the temperature range of 400–700°C are shown in Fig. 5a. The increase in the absorption value for the samples of SiO_2:TiO_2(B) composite in the wavelength range of 410–800 nm is caused by consolidation of TiO_2 nanoparticles in the pores of SiO_2-matrices due to possible formation of clusters from TiO_2 nanoparticles at the annealing of the composite. This effect is especially noticeable in SiO_2:TiO_2(B) composite annealed at 700°C for 4 hours (Fig. 5, spectrum 6): in this case there is observed a significant increase in the absorption of the composite samples from ~ 370 nm towards larger wavelengths. According to [20], TiO nucleation in TiO_2–SiO_2 films (synthesized from tetraethylorthosilicate and tetrabutyl titanate) occurs in the range 550–750°C.

As seen from the absorption spectra of SiO_2:TiO_2(B) composite (Fig. 5a), there is a shift of the edge of the fundamental absorption band in the composite relative to pure SiO_2-matrice by ~ 50 nm toward lower energies (i.e., to higher wavelengths). As is known, the position of the fundamental absorption edge of SiO_2:TiO_2(B) sample at 3.6 eV corresponds to the band gap for amorphous oxo-alkoxy titanium nanoparticles [14]. Annealing of the composite at temperatures from 400°C to 700°C did not lead to a significant transformation of the absorption spectrum of the sample (Fig. 5a, b). Such a fact

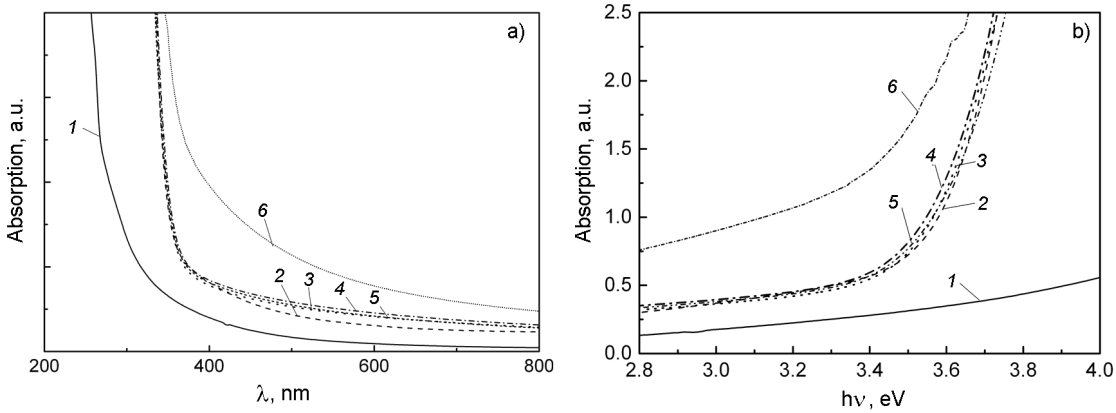

Fig. 5. Absorbance spectra of pure SiO_2-matrix of type (B) without TiO_2 (*1*), SiO_2:TiO_2(B) composite annealed at temperature of 60°C (*2*), at temperatures up to 400°C (*3*), 580°C (*4*), 700°C (*5*) and annealed at 700°C during 4 hours (*6*) depending on wavelength (a) and energy (b). Before saturation with TiO_2 all pure SiO_2-matrices were previously annealed at a temperature up to 700°C.

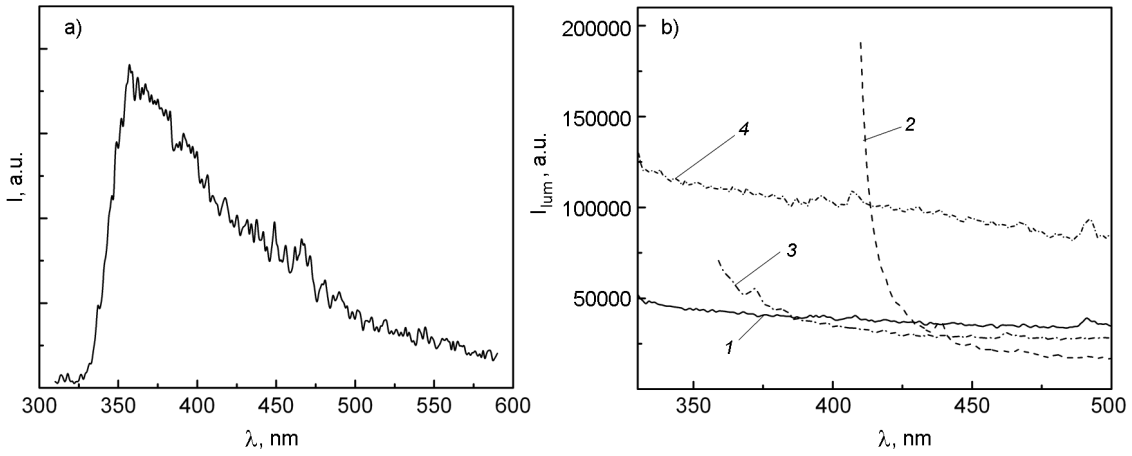

Fig. 6. Luminescence spectra of SiO_2:TiO_2 (B) composite, annealed at a temperature up to 700°C; λ_{ex} = 4.134 eV (300 nm). SiO_2-matrix synthesized with HF and before saturation with TiO_2 was previously annealed at a temperature up to 700°C (a); and luminescence spectra of pure SiO_2-matrices with a porosity of 23 % (1–3) and 55 % (*4*) (synthesized with HF and annealed at a temperature up to 650°C). SiO_2-matrices were excited at: λ_{ex} = 300 nm (*1*), λ_{ex} = 400 nm (*2*), λ_{ex} = 340 nm (*3*) and λ_{ex} = 300 nm (*4*) (b).

may testify to the absence of formation of a significant amount of the crystalline phase of TiO_2 [22].

Measurements of the photoluminescence spectra of pure SiO_2-matrix and of SiO_2:TiO_2 composite showed that for the pure matrix luminescence was absent (as in [12]). In the luminescence spectrum of the composite there was observed a broad peak caused by radiative recombination of electron-hole pairs in TiO_2 nanoparticles with a maximum at 362 nm (3.4 eV) [23] (Fig. 6a). This peak is most probably caused by electron transitions from deep traps inside the forbidden zone which are usually associated with disturbances of the structure of TiO_2 nanoparticles caused by oxygen vacancies. Such defects are formed during preparation of TiO_2 nanoparticles. A slight increase in the luminescence intensity in 2.7 eV (459 nm) region is probably bound up with luminescence of oxygen vacancies on the surface of TiO_2 nanoparticles [23]. This peak is absent in the luminescence spectra of TiO_2 nanoparticles with a minimum amount of oxygen vacancies, that, as a rule, agrees with the data in [24]. In addition, it is obvious that the high ratio of the surface-to-volume of TiO_2 nanoparticle ensures the existence of a large number of oxygen vacancies on its surface. In the literature there are various data on the bands in the luminescence spectrum of TiO_2 nanoparticles. For example, in [25] luminescence bands at 3.1, 3.19, 3.01 and 2.98 eV (at λ_{ex} = 330 nm) were observed for crystalline TiO_2 films annealed up to temperatures of 200°C, 300°C, 400°C and 500°C, respectively. Moreover, for amorphous TiO_2 membranes there was observed a broad luminescence band with a maximum at 3.3 eV under excitation by X-ray radiation with an energy of 450 eV [26]. As shown in [20], nanostructured titanium dioxide also may have a luminescence band in the range of 360–550 nm.

It should be noted that the pure SiO_2-matrices synthesized in this work (annealed in the temperature range of 500–700°C) do not exhibit intrinsic luminescence upon excitation of luminescence in the wavelength range of 300–400 nm (Fig. 6b). This distinguishes our matrices from the sol-gel films containing SiO_2, which photoluminescence the authors of [20] attribute to oxygen related defects on Si leading to a blue emission band. So, luminescence in pure sol-gel SiO_2 samples is probably influenced by the method of their preparation.

The annealing of the synthesized SiO_2:TiO_2 composite to 700°C during preparation of the samples for measurement of the luminescence spectrum was caused by the fact that further increase in the annealing temperature could result in a worsening of the quality of SiO_2-matrice.

The presented SiO_2:TiO_2 composites with TiO_2 nanoparticles and nanocrystallites in an amorphous highly porous matrices may be used as photocatalysts.

At the same time, the pores that remain in the composites after saturation of SiO_2-matrces with TiO_2 nanoparticles, may also cause light scattering. In the case of filling these pores with an optically transparent material, the scattering of light in the visible region of the spectrum can be reduced. Therefore, after filling these pores with polymethyl methacrylate (for example, polymerization of methyl methacrylate in the pores), light transmission by such a composite in the optical range can significantly rise. This makes it possible to use such a modified composite in photonics and may be a subject for further research.

4. Conclusions

SiO_2:TiO_2(A) and SiO_2:TiO_2(B) composites were obtained by saturation of pure SiO_2-matrices (with a porosity of ~ 30 % and ~ 42 %, respectively) with TiO_2 suspension and subsequent annealing at temperatures up to 700°C. Annealing of SiO_2:TiO_2(B) composite in the temperature range of 400–700°C increased the absorption in the visible spectral range, which might be caused by agglomeration of TiO_2 nanoparticles in the pores of SiO_2-matrices. The observed luminescence of TiO_2 nanoparticles in SiO_2:TiO_2(B) composite in the range of 360–460 nm (at λ_{ex} = 300 nm) is due radiative recombination of charge carriers at deep defect levels formed by oxygen vacancies. The presence of diffraction rings in the electron microdiffraction images of the samples of SiO_2:TiO_2(A) and SiO_2:TiO_2(B) composites points to the presence of TiO_2 crystallites. However, the low (less than 1 %) concentration of titanium relative to silicon in the composite did not make it possible to reveal the presence of crystalline TiO_2 phase in the annealed composites by powder X-ray diffraction method. TiO_2 is present in SiO_2:TiO_2(A) and SiO_2:TiO_2(B) composites based on highly porous SiO_2-matrices in the form of crystallites and in amorphous state, which allows to use them as photocatalysts.

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