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The Radiation Peculiarities of Nanoscale SnO_2 in a Porous Matrix

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The features of luminescent properties of an ensemble of tin dioxide nanoparticles created inside various types of porous silicate glass matrices under various thermosynthesis conditions are studied. It was demonstrated that the highest intensity of radiative recombination is inherent to the system formed in finely porous silicate glass with residual silica gel in the pores. Silica gel in this case prevents the aggregation of SnO_2 nanoparticles. For the all types of matrix, the luminescence energy is less than the fundamental SnO_2 energy gap, which may indicate a trap-like luminescence character of these systems. It was established an occurrence of at least two types of recombination centers – acceptors close to the valence band. The luminescence intensity varies depending on the content of the precursor in the initial solution to obtain samples. Its maximum is observed at 5-7 % tin chloride in the initial solution. The specified method of ensemble creation corresponds to the greatest width of the luminescence spectral lines, which is inherent to the intensity of radiative recombination. The smallest width of the spectral line corresponds to large concentrations close to those at which the $SnCl_4$ alcohol solution becomes a strong glass adhesive. At these concentrations the solution already begins to glue the silica gel particles, freeing up space for the further formation of aggregations after the thermosynthesis reaction. In this case, the aggregation is intensive. In ensembles of SnO_2 nanoparticles created in porous glass depleted in silica gel, nonradiative recombination predominates due to leakage channels through aggregations formed during thermosynthesis in the absence of an insulating substance. The study results can be used to create luminescent gas sensors based on SnO_2.

Keywords: Tin dioxide, Porous matrix, Silicate glass, Luminescence, Nanoparticles ensembles.

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1. THE PROBLEM STATEMENT

The recently discovered features of photoluminescence of nanoscale forms of tin dioxide [1, 2] have attracted considerable interest associated with the expansion of its application as photoluminescent active elements of sensors [3-5]. Dispersion of tin dioxide to nanometer sizes, in the best way, facilitates deviation from stoichiometry and the formation of interstitial cations and Schottky anion defects. Just in the presence of such defects in the crystal structure, the electrophysical and luminescent properties of this substance manifest themselves in the best way [6]. This dispersion can be achieved by fixing the nanoscale formations of tin dioxide in a suitable matrix. To prevent nonradiative recombination, to reduce the quantum yield of luminescence, it is desirable to isolate individual nanoparticles. This will prevent their further aggregation, and, as is known [7], just the aggregations are the main leakage channels. As it is stated in [8], the critical size of SnO_2 nanoparticles should be considered of 25 nm, and the excess of it leads to the prevalence of bulk properties. Thus, to obtain stable properties of the studied material, it is necessary to ensure the particle size of the ensemble within the specified limits.

2. METHODS AND SAMPLES

An effective technology for the formation of a large canonical ensemble of nanoparticles is based on the impregnation of a suitable model medium with a solution of the corresponding substance followed by annealing, which contributes to a uniform distribution of nanoparticles in the ensemble [7, 9]. Porous silicate glass plays a rather good role as a model medium for creating ensembles of nanoparticles [7, 9, 10]. The process of nanoparticle formation can be controlled due to the existence of several types of glasses [7, 9, 11, 12] and the possibility of selecting a suitable concentration of the impregnating solution and annealing parameters.

The types of silicate porous glass differ in pore sizes and the presence or absence of residual silica gel inside them. Four of them do not luminesce in the spectral region in which SnO_2 reliably luminesces, hence, they may be used as a matrix. These glasses are conventionally called glasses of A, B, C and D types [7, 9]. Glasses of A and C types differ in pore sizes and, due to their formation peculiarities, contain residual silica gel in them. This formation in its chemical composition (SiO_2) does not differ from the porous framework, but differs from it in structure, since it is small sand-like particles. If, by processing in a KOH solution [13], silica gel is removed from type A glass, it turns into B type glass, and in the case of the mentioned treatment of C type glass, it turns into glass of type D. Glasses A and B are finely porous, while glasses C and D are large porous [9].

The porous glass matrix direct impregnation with SnO_2 solution is impossible, since this substance is insoluble in all solvents that do not destroy the specified model medium. However, it is possible to synthesize tin dioxide nanoparticles directly in the matrix's pores by impregnating it with the soluble component of the reaction. Such a substance is $SnCl_4$. Tin chloride is highly soluble in alcohol and can be converted into SnO_2 by thermosynthesis [14]. Thermosynthesis is possible at sufficiently low temperatures (about 400 °C), which do not destroy the matrix [13]. At the

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same time, the process is long enough (several hours), but the indicated thermosynthesis temperature promotes the formation of smaller SnO_2 particles [15], and the presence of residual silica gel in the gaps prevents their aggregation [7].

The luminescence spectra of the samples obtained upon excitation by an LCS-DTL-374QT ultraviolet laser (wavelength $\lambda = 355$ nm, power 15 mW) were recorded on a setup consisting of an SF-4 quartz monochromator, an FEU-79 photomultiplier with a sensitivity of 280-850 nm, as a photodetector, and a selective amplifier, was synchronized with the frequency of the exciting laser. The result was transmitted via an analog-to-digital converter using the USB-oscillography program to a computer monitor.

3. RESULTS AND DISCUSSION

In order to select the type of glass, which is used as a matrix for creating the SnO_2 nanoparticles' ensemble, the most significant luminescent response should be. Each of the four mentioned glass types was impregnated with an alcohol solution of $SnCl_4$ with one and the same concentration of 5 % during a day and then annealed at 400 °C for three hours. The photoluminescence (PL) spectra of all ensembles of SnO_2 nanoparticles created in this way, regardless of the type of matrix, are Gaussian-like (Fig. 1).

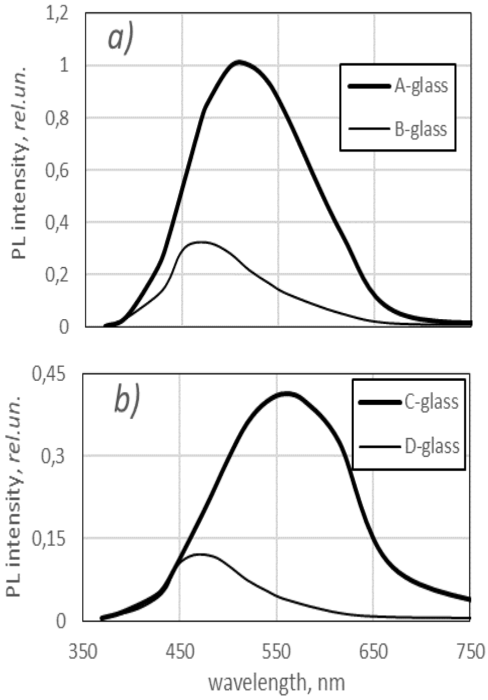

Fig. 1 – The PL spectra of SnO_2 nanoparticle ensembles in fine porous (a) and large-porous (b) glasses

A comparison of the PL spectra of ensembles of SnO_2 nanoparticles based on glasses A and C demonstrates significantly lower luminescence intensity and a shift to lower energies when using a large pore matrix. It can be assumed that nanoparticles with sizes exceeding critical 25 nm are more likely to form in its pores, so that bulk properties prevail in them [8]. Thus, the contribution of small nanoparticles, which corresponds to the highest luminosity, is minimal in type C glass and this affects the intensity of the PL spectrum. In addition, larger particles usually correspond to a long-wavelength shift of the maximum of the spectrum, which confirms the assumption made.

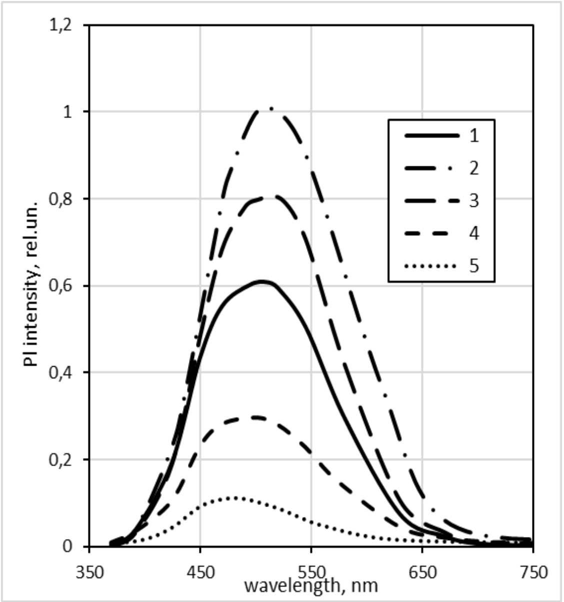

Fig. 2 - Dependence of the PL spectra of SnO_2 nanoparticle ensembles in glass A on the concentration of saturated $SnCl_4$ solution

The spectra of the ensembles formed in matrices based on glasses B and D depleted in silica gel have significantly lower luminescence intensity than those formed in matrices untreated by KOH solution. In addition, they are located inside the spectra of ensembles created on the basis of glasses A and C, respectively, and their maxima are shifted to the short-wavelength side. Therefore, it can be stated that the depletion of the pores of the matrix with silica gel promotes the aggregation of formed nanoparticles. And, since aggregations are leakage channels [7], in the case of SnO_2 nanoparticles, less energetic quanta recombine through them in a nonradiative manner.

For comparison, the half-width of the spectral lines of ensembles of SnO_2 nanoparticles formed at a 5 % concentration of an impregnating $SnCl_4$ solution in all four types of glasses is shown in Table 1.

Table 1 – The spectral lines half-width of SnO_2 nanoparticles ensembles in various types glasses

Glass type	A	B	C	D
The half-width of the spectral lines, nm	165	125	140	125

Since the broader spectral line corresponds to a shorter carriers' lifetime in the system, which in turn corresponds to more intensive radiative recombination, it can be stated that non-radiative recombination prevails in glasses depleted of residual silica gel. This confirms that the presence of residual silica gel in the pores prevents the aggregation of nanoparticles.

Thus, type A glass is a model medium in which the best luminescent response is observed for SnO_2 nanoparticles ensemble. Despite this, in order to determine the optimal technological parameters for the formation of SnO_2 nanoparticles ensemble, the set of samples were prepared from impregnating $SnCl_4$ solutions with gradually varying concentrations.

It should be noted that $SnCl_4$ is highly soluble in ethanol, however, such a solution in concentrations exceeding 30 % destroys the matrix [9]. Therefore, it was advisable to create a set of samples consisted of type A porous glass plates with sizes of 5×5×0.5 mm, saturated with solutions of $SnCl_4$ in ethanol with a concentration lower than 30 %, and subjected to annealing for 3 h at 400 °C. Conventionally, samples are designated as 1, 2, 3, 4, and 5, which correspond to concentrations of 2.5 %, 5 %, 7.5 %, 12.5 %, and 25 %, respectively. The PL spectra of all samples of the set are shown in Fig. 2. They turned out to be Gaussian-like and the luminescence intensity magnitudes differed significantly. At the same time, the positions of their maxima changed insignificantly. Despite this, these shifts correlate with the intensity of the glow.

From Fig. 2 it can be seen that the high concentrations of the saturating solution correspond to rather low luminescence intensity. It increases significantly at approaching a concentration of 7.5 %, and for concentrations below 5 % it decreases again. A similar pattern was observed for tin dioxide nanoscale film, created by the sol-gel method, when luminescence maximum also corresponded to the average concentration of the precursor in the solution of about 5 % [16].

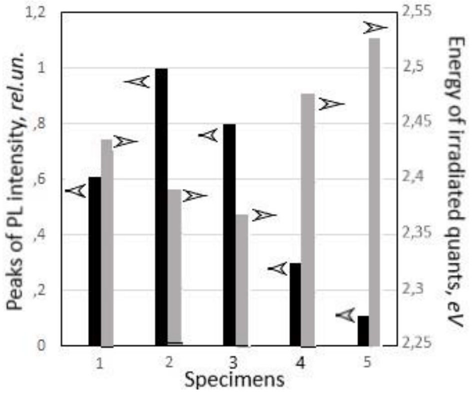

Fig. 3 - The luminescence maximum intensities of SnO_2 nanoparticle ensembles in type A glass (left scale) and the most probable energies of radiation quanta (right scale) for different samples

In the histogram, Fig. 3, the luminescence intensity maxima for SnO_2 nanoparticle ensembles (left scale) and the corresponding probable quantum radiation energies (right scale) are compared for all samples' sets. The latter are obtained by a simple recalculation on the basis that the energy of the radiation quanta is proportional to the position of the luminescence maximum. It can be seen that the lowest luminescence intensity corresponds to the highest energy of the radiation quantum. For all cases, the luminescence energy is less than the fundamental SnO_2 energy gap (3.54 eV), which may indicate a trap-like luminescence character.

At all concentrations of $SnCl_4$ solutions, which are present in the samples' set, the PL spectra of the formed SnO_2 nanoparticles ensembles have a broad-band character (Fig. 2). This indicates the presence in the system of at least two acceptor type recombination centers close to the "ceiling" of the valence band. It can be seen that together with the increase of impregnating solution concentration there is a relative growth of short wave band contribution to the total radiation, with a simultaneous decrease of both band intensities. The half-widths of the spectral lines for the entire sample set are shown in Table 2.

Table 2 – The spectral line half-widths for SnO_2 nanoparticle ensembles at different concentrations of impregnating solution

Samples	1	2	3	4	5
Concentration $SnCl_4$, %	2.5	5	7.5	12.5	25
The half-width of the spectral lines, nm	145	165	155	135	120

From Table 3 it follows that the smallest width of the spectral line corresponds to large concentrations close to those at which the $SnCl_4$ alcohol solution becomes a strong glass adhesive [9]. It should be supposed that at these concentrations the solution does not break the matrix yet, but it already begins to glue the silica gel particles, freeing up space for the further formation of aggregations after the thermosynthesis reaction. In this case, the aggregation is intensive. The spectral lines half-width reduces while reduction of the concentration of the impregnating solution to 2.5 % is probably related simply to a decrease in the total carrier concentration in the system. The absolute luminescence maximum depending on random factors is in the concentration range from 7.5 % to 5 %. This follows from the fact that these concentrations of the $SnCl_4$ forming solution correspond to almost the same energy of the emitted quanta, namely 2.37-2.39 eV.

4. CONCLUSIONS

As a result of studies of the luminescence of nanoscale tin dioxide in the porous matrix, the following features are established:

– the best luminescent response is obtained by the ensemble of SnO_2 nanoparticles formed in fine porous silicate glass with residual silica gel in the pores by impregnating it with an alcoholic solution of $SnCl_4$ with a concentration in the range of 5-7.5 % followed by thermosynthesis;

– the applied method of ensemble creation corresponds to the greatest width of the luminescence spectral lines, which is inherent to the intensity of radiative recombination;

– most likely, the luminescence of the specified system has a trap character, with at least two types of recombination centers – acceptors close to the valence zone;

– in ensembles of SnO_2 nanoparticles created in porous glass-depleted silica gel, the non-radiative recombination prevails, due to leakage channels through aggregations, which are formed in the process of thermosynthesis due to the absence of an insulating substance.

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Особливості випромінювання нанорозмірного SnO_2 в пористій матриці

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Досліджено особливості люмінесцентних властивостей ансамблю наночастинок діоксиду стануму, створеного всередині матриць шпаристого силікатного скла різного типу при різних умовах термосинтезу. Продемонстровано, що найбільша інтенсивність випромінювальної рекомбінації притаманна системі, сформованій у дрібношпаристому силікатному склі із залишковим силікаґелем у шпаринах. Силікагель у цьому випадку запобігає агрегуванню наночастинок SnO_2. Для усіх типів матриці енергія світіння виявилася меншою від фундаментальної енергетичної щілини SnO_2, звідки зроблено висновок, що люмінесценція зазначеної системи має пастковий характер. Встановлено наявність принаймні двох типів центрів рекомбінації, що є близькими до валентної зони акцепторами. Інтенсивність люмінесценції змінюється залежно від складу прекурсору у вихідному розчині для здобутих зразків. Її максимум спостерігається при 5-7 % хлориду олова у вихідному розчині. Зазначеному режиму створення ансамблю відповідає найбільша ширина спектральних ліній люмінесценції, що притаманне найбільшій інтенсивності випромінювальної рекомбінації. Найменша ширина спектральної лінії відповідає великим концентраціям, найближчим до тих, за яких спиртовий розчин $SnCl_4$ перетворюється на міцний клей для скла. за цих концентрацій розчин починає склеювати частинки силікаґелю, вивільнюючи місце для подальшого формування агрегацій після реакції термосинтезу. У цьому випадку агрегування виявляється найінтенсивнішим. У ансамблях наночастинок SnO_2, які створено у шпаристих стеклах, що збіднені силікагелем, домінує невипромінювальна рекомбінація, що є обумовленою каналами витоку крізь агрегації, які утворюються підчас термосинтезу у відсутності ізолюючої речовини. Результати дослідження можуть бути використаними для створення люмінесцентних газових сенсорів на базі SnO_2.

Ключові слова: Діоксид олова, Пориста матриця, Силікатне скло, Люмінесценція, Ансамблі наночастинок.