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Atomic single bubble sonoluminescence of ytterbium in a colloidal suspension

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For the first time, atomic single-bubble sonoluminescence of Yb in a colloidal suspension in dodecane of SiO₂ nanoparticles containing YbCl₃ was recorded. A spectrum was obtained containing Yb, Yb⁺ lines in the region of 300–550 nm, together with SiO lines, due to the entry of nanoparticles into the bubble during sonolysis of the suspension. The lower limit of determination of ytterbium in the initial aqueous solution of YbCl₃ used for depositing onto nanoparticles, according to the intensity of the analytical line at 399 nm in this spectrum, is $3 \cdot 10^{-3}$ mol/l. By comparing the experimental and temperature-dependent calculated spectra of ytterbium, we found the electronic temperature in the nonequilibrium plasma that arises during bubble collapse, where Yb atoms emit light: $T_e = 7000 \pm 500$ K.

Keywords: single-bubble sonoluminescence, silicon dioxide, ytterbium, colloidal suspension.

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Recently, a new method of luminescence analysis is developed — sonoluminescence spectroscopy [1,2]. It is based on obtaining spectra of ultrasonic sonoluminescence (SL) in solutions and determining the characteristics of luminescent substances from them (identifying and determining their concentration, determining the parameters of the radiating medium). The method was initiated by the discovery of alkali metals atomic SL of alkali metals in aqueous solutions [3]. Then the characteristic lines of atomic SL were discovered in other metals and used to analyze the temperature and pressure of nonequilibrium plasma that appears in a liquid under the action of ultrasound in cavitation bubbles, where the metal atoms, that penetrated into them from the solution, luminesce [4]. Later, SL was also found for multi-charged ions of lanthanide (Ln^{3+}) [5], uranyl (UO₂²⁺) [6], organic phosphors [7]. Undoubtedly, all these cases of SL are suitable for the luminescent determination of the corresponding compounds, but so far this method is most developed for the analysis of elements — metals, whose atomic spectra till recent time were obtained only using the method of multibubble sonoluminescence (MBSL) in solutions [1,2]. However, it was shown that the best results in obtaining characteristic spectra are obtained by the method of single-bubble sonoluminescence in motion mode (SBSL-MM) in solutions [8], and also, as established later, the SBSL-MM method in colloidal suspensions (SBSL-MM-CS), where the determined elements enter the bubble plasma as part of nanoparticles [9]. The use of this method makes it possible to obtain spectra at lower concentrations of the elements to be determined than with MBSL, and the spectra of elements not detected by MBSL.

The possibility of obtaining the characteristic spectra of SL elements is not only determined by their concentration

in solution, but also depends on the efficiency (cross section) of collisional excitation of luminescent transitions in a bubble plasma, as well as on other factors. Thus, when considering the spectra of Ce³⁺, Pr³⁺, Gd³⁺, Tb³⁺, obtained by SBSL-MM CS (in a suspension of SiO₂ nanoparticles containing LnCl₃), quasi-lines of 4*f*–4*f* transitions for Gd³⁺ and Tb³⁺ were registered. However, the 5*d*–4*f* transition bands for the Ce³⁺ and Pr³⁺ ions were not registered due to the lower (by an order of magnitude or more) efficiency of collisional excitation for the 4*f*–5*d* transitions than for transitions inside the electron shell 4*f*–4*f* [10]. Yb³⁺ quasi-lines were also not detected, despite the *f*–*f* type of excitation of this ion, but here, as we believe, already in view of the lower quantum yield of its luminescence compared to the yields for Gd³⁺, Tb³⁺ and lower efficiency of Yb³⁺ luminescence detection in the IR region. We also considered the possibility of detecting atomic lines of lanthanides in solutions and suspensions containing LnCl₃, since it is known that during SL in cavitation bubbles many multiple-charged metal ions are recovered, and just atomic lines are registered [2]. In the paper [10] the Ce, Pr, Gd, Tb atomic lines were not registered. The main reason for this, apparently, is also the low efficiency of collisional excitation of the corresponding transitions of these elements under sonoluminescent plasma conditions. Taking into account the data on the intensities of the analytical lines of the elements that appear under the conditions of electric discharge plasma [11], it was found that the intensity of the lines of these lanthanides is about 200 conventional units (compared to 9000 conventional units for the lines of easily detectable alkali metals). Among all lanthanides, only ytterbium can be distinguished with the

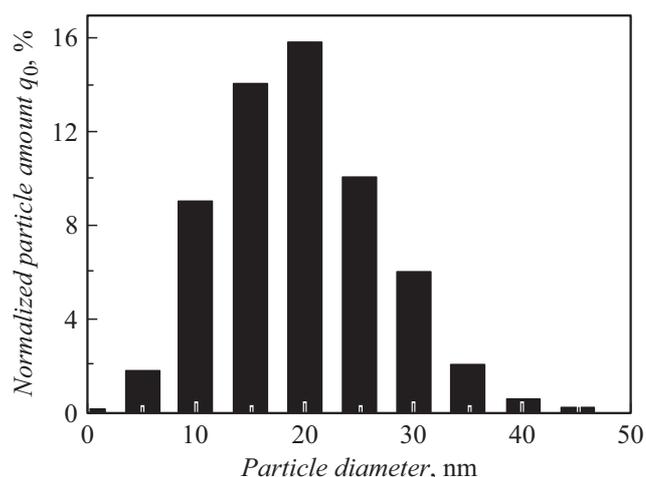


Figure 1. Size distribution of silica nanoparticles saturated with ytterbium chloride in dodecane. Laser analyzer Sald-7101 Shimadzu.

highest this index (1000 conventional units), which allowed us to hope for the detection of Yb atomic lines.

In connection with the above, the subject of this paper is the determination of characteristic atomic lines in the sonoluminescence spectrum of ytterbium, obtained using the SBSL-MM CS method, as well as carrying out certain types of spectroscopic analysis with it: estimation of the lower limit of the concentration of YbCl_3 concentration in the analyzed solution and the electronic temperature reached in the nonequilibrium plasma of the bubble generating sonoluminescence.

In the paper dodecane (Acros) served as the dispersing phase of the colloidal suspension. Bidistilled water and YbCl_3 „xch“ were used to prepare the initial aqueous solution. According to the method described in paper [10], the micromesoporous powder SiO_2 (0.2 g) was saturated

with lanthanide ions by adsorption from the initial solution (3 ml, 38 mg $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$), dried by vacuum and dispersed for 45 min in 100 ml dodecane at multibubble sonolysis at ultrasound frequency of 20 kHz, followed by filtration to isolate the final fraction of colloidal suspension with nanoparticles smaller than 50 nm. The method for obtaining single-bubble sonoluminescence in a spherical resonator is described in [9,10]. The absorbed power of ultrasound when recording the SL spectra was about 5 W. All spectra, obtained using scanning monochromator MDR-206 and photon counter PCU-100, were corrected for the spectral sensitivity of the recording equipment.

Fig. 1 shows the size distribution of SiO_2 nanoparticles obtained by ultrasonic dispersion in dodecane with deposited YbCl_3 , the average size of which was 15–25 nm.

Fig. 2, *a* shows the SBSL-MM spectrum of the synthesized colloidal suspension averaged over the results of ten surveys at a spectral resolution of $\Delta\lambda = 1$ nm. At this resolution, the Yb and Yb^+ lines at 289, 298, 328, 346, 370, 399, and 555 nm are clearly identified by [11] in the spectrum. Along with the atomic lines of ytterbium, this spectrum also contains low-intensity emission lines of the SiO molecular emitter (the product of decomposition of SiO_2 in bubble), identified by [12]. For an immobile bubble under given shooting conditions, atomic and molecular emitters are not detected in the SBSL spectrum. Only a broadband glow continuum of the bubble plasma is recorded, which is present with practically unchanged intensity and shape in the SBSL-MM spectrum as well, against which background (the continuum is not shown in Fig. 2, *a*), and a line spectrum is observed.

Using the method of [13] the calculated temperature-dependent luminescence spectra of ytterbium were obtained. The calculated spectra of ytterbium (for Yb and Yb^+ lines) at temperature of 7000 K (Fig. 2, *b*) most closely match the experimental spectrum (Fig. 2, *a*). From a comparison of the spectra the electron temperature

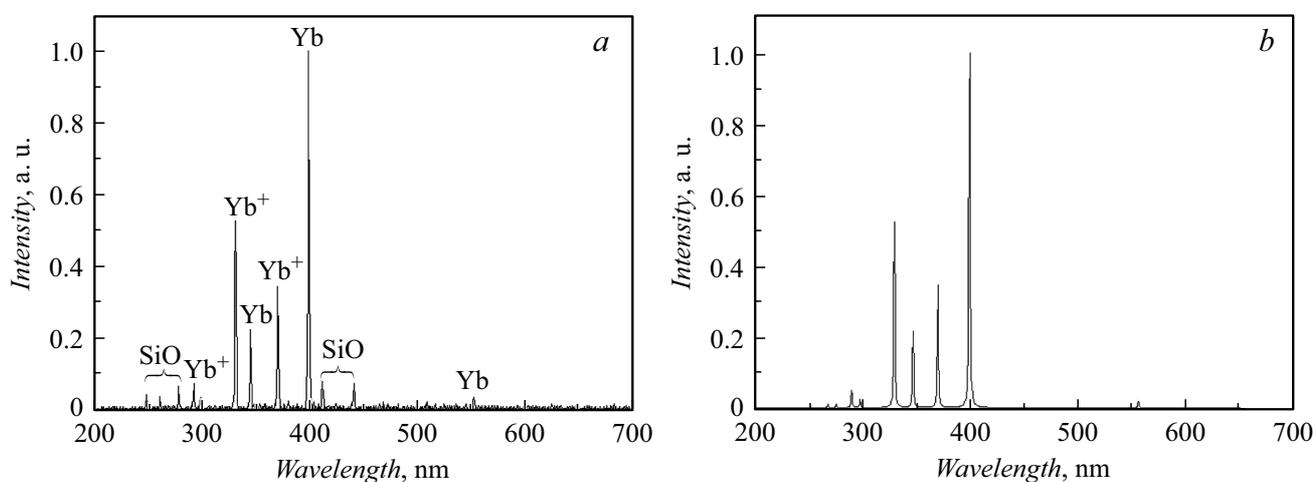


Figure 2. *a* — SBSL-MM spectrum of colloidal suspension of SiO_2 nanoparticles containing ytterbium (minus the background continuum of the bubble plasma glow in dodecane). The concentration of YbCl_3 in the initial aqueous solution for preparing the colloidal suspension is $3.3 \cdot 10^{-2}$ mol/l. *b* — calculated spectrum of Yb and Yb^+ at temperature of 7000 K, obtained by the methodology [13].

reached in the nonequilibrium plasma occurred during bubble collapse, where ytterbium atoms and ions emit light falling into a bubble in dodecane with SiO₂ nanoparticles, is: $T_e = 7000 \pm 500$ K.

Based on the obtained linear dependence of the intensity of the analytical line Yb at 399 nm in the OBSL-MM spectrum on the concentration of ytterbium chloride in the initial aqueous solution with which the nanoparticles were impregnated, the limit of ytterbium detection in this solution was determined: $3 \cdot 10^{-3}$ mol/l. Note that the intensity of this ytterbium line turned out to be below the detection threshold in our experiments relating MBSL in aqueous solutions (at an absorbed ultrasound power of 30 W and other recording conditions similar to the case of SBSL) even at a concentration of YbCl₃ equal to 0.1 mol/l.

Thus, the characteristic atomic spectrum of ytterbium suitable for the purposes of sonoluminescent spectroscopic analysis was recorded for the first time using the SBSL-MM method for colloidal suspensions. The limit of ytterbium determination in aqueous solutions of ytterbium chloride by the proposed method was $3 \cdot 10^{-3}$ mol/l. The electron temperature is determined, that is reached in the nonequilibrium plasma occurred during bubble collapse, where ytterbium atoms emit light falling into a bubble with SiO₂ nanoparticles, is: $T_e = 7000 \pm 500$ K.

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Conflict of interest

The authors declare that they have no conflict of interest.

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