Production of copper nanoparticles in the process of target ablation by radiation Cr^{3+}:$BeAl_2O_4$ laser

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Abstract. The work is devoted to the synthesis of nanoparticles in the process of ablation of a copper target in a liquid by repetitively pulsed laser radiation. It has been noted that nanomaterials based on certain metals have unique physical and chemical properties. This ensures their use in various applications. In particular, copper nanoparticles are successfully used in medicine and biochemistry. To carry out the synthesis of copper nanoparticles, a previously developed Cr^{3+}:$BeAl_2O_4$ laser is used. The laser is based on a plane-parallel resonator with a dispersive prism. Using a prism, the radiation wavelength is smoothly adjusted. To carry out copper ablation, the laser generation wavelength was tuned to 740 nm. It has been shown that when a target is exposed to a microsecond laser pulse consisting of a train of short pulses, copper nanoparticles of various sizes are formed. Comparison of the results with the results of previous works shows that exposure of the target to radiation with a shorter wavelength, commensurate with the energy density of the train and similar spatial parameters leads to a decrease in the average size of the synthesized nanoparticles.

1 Introduction

Today, solid-state lasers, along with other types of lasers, form the basis of photonics - the modern field of generation and conversion of electromagnetic radiation, the quanta of which are photons. The development of this area has led to the development of many areas for the use of lasers in mechanical engineering, ecology, communication systems, and materials processing technologies. Almost since the creation of solid-state lasers, the results of their use in medicine have been known. In particular, lasers generating radiation in the near-IR region of the spectrum are used in surgery and cosmetology. Radiation with

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wavelengths of 0.83 μm, 0.89 μm and 0.785 μm are promising for the treatment of numerous skin diseases [1]. A promising direction for using solid-state laser radiation is laser ablation of materials in liquid, which is used to form nano-sized materials. Nanomaterials based on certain metals (for example, silver, gold, etc.) have a number of unique combinations of new physical and chemical properties [2]. Copper nanoparticles are of particular interest today. In particular, their use is relevant in medicine and biochemistry [3], in the production of conductive films, in the creation of bactericidal agents [4] and nonlinear devices [5]. When using this method, chemically pure substances are formed in a short time, which can be ready for further use [6]. In this regard, improving the process of forming copper nanoparticles with various laser parameters, including smaller sizes, by laser ablation of the material in a liquid is relevant. Therefore, we set ourselves the task of conducting experimental studies of the dependence of the size of formed copper nanoparticles on the wavelength of the applied laser radiation.

2 Materials and methods

2.1Analysis

In most cases, the possibility of using a laser in any field depends on the availability of technical solutions for generating radiation with the required wavelengths. In particular, for most metals, including copper, the absorption coefficient is inversely proportional to the radiation wavelength. Therefore, for processing such materials, it is preferable to use radiation with a shorter wavelength. Therefore, in this work, we implemented a tuning of the wavelength of the Cr^{3+}: $BeAl_2O_4$ laser radiation to the short-wavelength region of the spectrum. Generation of radiation in the required spectral range can be realized by tuning its wavelength. This, in turn, is carried out either with the help of crystals with nonlinear optical properties, or with the use of spectral-selective, dispersive optical elements in the resonator. Classical traditional methods for tuning and stabilizing the wavelength of laser radiation in the IR range of the spectrum are based on the use of a dispersive prism in the resonator, one of the surfaces installed at an angle close to the Brewster angle relative to the laser beam. The selective characteristics of resonators with a prism are primarily determined by its angular dispersion, which is determined by the beam path in it and the dispersion of the material. Therefore, prisms made from a material with greater dispersion should provide greater spectral selectivity. Optical materials operating in the visible and near-IR spectral range and having high dispersion and transmission values include glasses of the TF series, including N-SF.
Taking into account the relation:

$$\frac{\partial\theta}{\partial n} = \frac{\sin A}{\cos\alpha_1 \times \cos\alpha_2} \quad (1)$$

where: $\alpha 1$ and $\alpha 2$ are the angle of refraction of radiation by the first and second faces of the prism, respectively, the refractive angle of prism A, the faces of which are oriented at the Brewster angle αBr to the optical axis of the resonator, can be determined by the formula:

$$A = 2 \times arcsin\left[\frac{1}{\sqrt{n^2+1}}\right] \quad (2)$$

The refractive index of N-SF glass for the main wavelength of laser radiation on Cr^{3+}: $BeAl_2O_4$ (750 nm), according to the values of the dispersion formula coefficients, is 1.74. Substituting this value into (2), we obtain that the refractive angle of the prism will be 59.7 degrees. The bandwidth of a circular path around the resonator can be determined by the formula:

$$\delta\lambda_{pr} = \frac{\lambda}{2\times r} \times \left(\frac{dn}{d\lambda}\right)^{-1} \times \frac{\cos\alpha_{Br}\times\cos\left(\frac{A}{2}\right)}{2\times\sin A} \quad (3)$$

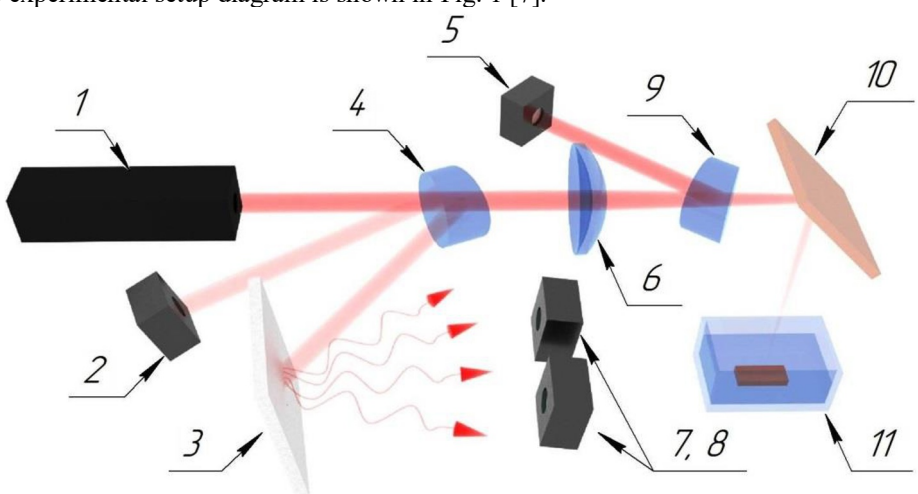
where: r = 3 mm – radius of the radiation beam, λ = 750 nm – main wavelength of laser radiation. Calculation according to (3) shows that the bandwidth will be equal to 0.27 nm. In this case, the resolution of the prism will be ≈2800. Considering that the resolution is:

$$R = L \times \frac{dn}{d\lambda} \quad (4)$$

we find that the size of the base (base) of the prism L must be no less than ≈24 mm. Thus, to adjust the wavelength of laser radiation in the range of 720-800 nm, approximately corresponding to the gain band, it is proposed to use a prism made of N-SF glass with a refractive angle of ≈60 degrees and a base size of at least 24 mm.

2.2 Experimental part

In this work, to adjust the laser radiation wavelength, we used a commercially available prism with a refractive angle of 60 degrees and a base size of 25 mm, made of N-SF11 glass (SCHOTT). The prism material has high values of dispersion, refractive index at the operating wavelength (1.77) and transmittance (0.985 with a thickness of 25 mm). The wavelength of the generated radiation was adjusted by changing the angle of rotation of the blind resonator mirror. The wavelength tuning range was 705-800 nm.
The experimental setup diagram is shown in Fig. 1 [7].



1 – laser on Cr^{3+}: $BeAl_2O_4$, 2 – pyroelectric converter PE-25 (Ophir), 3 – diffuse screen, 4, 9 – optical wedge, 5 – Pyrocam III laser beam profile analyzer (Ophir), 6 – lens, 7 – OD-08A photodetector (Avesta), 8 – HR4000 spectrometer (Ocean Optics), 10 – rotary mirror, 11 – cuvette with a copper target.

Fig. 1. Experimental setup diagram [7].

To measure the energy of a microsecond train, a PE-25 pyroelectric converter with a spectral sensitivity range of 0.15-3 μm and a measurement range of 8 μJ-10 J was used. The wavelength and duration of the radiation train were measured using an HR4000 spectrometer (resolution no worse than 1 nm) and a photodetector OD-08A (time constant 0.5 ns) with a Rigol oscilloscope, respectively, by recording radiation reflected from a diffuse screen. The energy density distribution and cross-sectional diameter of the laser beam were assessed by a PY-III HR laser beam profile analyzer.

We established that for copper at the target-liquid interface, a plasma torch is formed when exposed to radiation with a wavelength of 750 nm and a train energy density of 52 J/cm^2. In this case, the radiation intensity distribution over the beam cross section corresponded to the Gaussian distribution; the beam diameter on the target at the level 1/e^2 from the maximum was 180 µm. The average copper particle size was 141 nm. Varying the parameters of the applied laser radiation makes it possible to change the parameters of the synthesized nanoparticles. In particular, work [8] demonstrated an increase in the average size and fragmentation of the resulting particles when varying the parameters of the laser pulse, including the radiation energy density on the sample.

In this work, we used the experimental approach described in [7] and the sample was exposed to periodic pulsed laser radiation with a wavelength of 740 nm. The energy density of the radiation train was about 47 J/cm^2. The diameter of the beam on the target at the level 1/e^2 from the maximum was 180 µm, the spatial profile of the beam corresponded to the Gaussian distribution. The duration of the laser pulse train was about 120 µs. As a liquid, similarly as in [7], we used distilled water. The experimental procedure is described in detail in [7].

3 Results and discussion

As a result of laser exposure, a one-component colloidal solution of copper nanoparticles was formed (Fig. 3a) with an average size of about 129 nm. Particle size was determined using a Horiba LB-550 laser particle size analyzer. A histogram of the size distribution of formed copper particles is presented in Fig. 2.

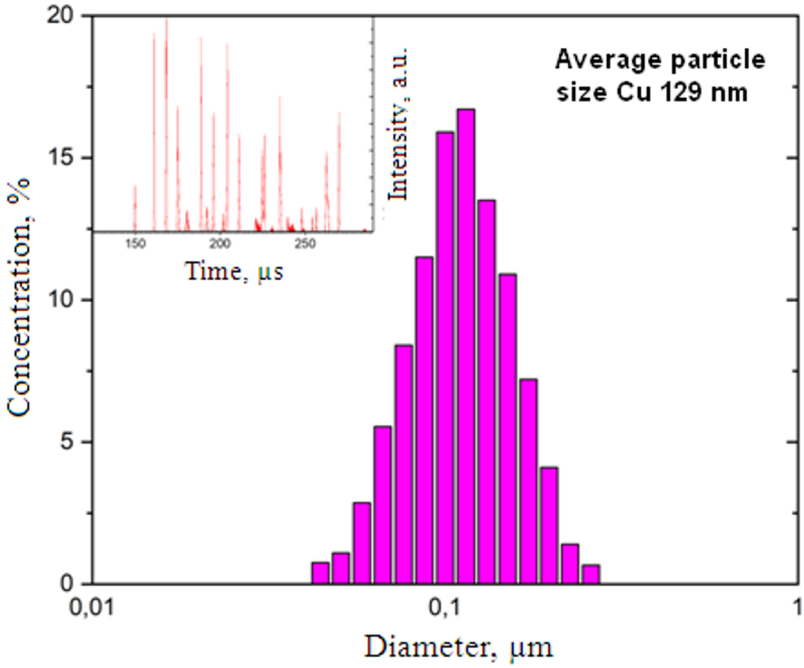


Fig. 2. Histogram of copper particle size distribution.

The experimental results show that the transition to exposing the target to radiation with a shorter wavelength, comparable to the train energy density and similar spatial parameters leads to a decrease in the average size of synthesized nanoparticles. In particular, when a target is exposed to radiation with a wavelength of 750 nm, nanoparticles are formed, the

average size of which is 141 nm [7], when exposed to radiation with a wavelength of 740 nm, the average size of synthesized nanoparticles is 129 nm. Tuning the lasing wavelength to the short-wavelength region (less than 740 nm) of the spectrum was accompanied by an intense decrease in the energy density of the radiation train, which limited the efficiency of nanoparticle formation.

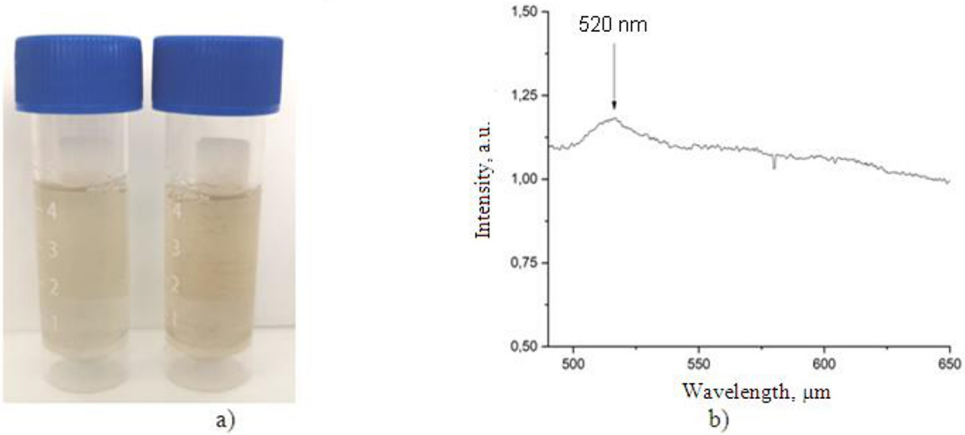


Fig. 3. One-component copper solutions –a) and absorption spectrum of the solution –b)

The absorption spectrum of colloidal solutions was determined by spectrophotometry. The absorption peak of colloidal solutions with synthesized copper nanoparticles was in the region of ~520 nm (Fig. 3b). Similar spectrophotometric results are described in works [5, 6] on the study and production of copper nanoparticles by laser ablation in a liquid.

4 Conclusions

In this work, we experimentally demonstrate the possibility of forming copper nanoparticles with an average size of 129 nm by ablation of a copper target in a liquid by periodically pulsed radiation from a Cr^{3+}: $BeAl_2O_4$ laser with a wavelength of 740 nm. The energy density of the acting radiation train was about 47 J/cm^2. To implement this mode of radiation generation, a dispersive prism is included in the cavity of the previously developed Cr^{3+}: $BeAl_2O_4$ laser. Thus, the work implemented a laser ablation mode of a copper target in a liquid, in which nanoparticles with an average size of 129 nm are formed. It has been established that exposure of a target to radiation with a shorter wavelength, commensurate train energy density, and similar spatial parameters leads to a decrease in the average size of synthesized nanoparticles.

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