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Effect of buffer gas pressure on the cooling rate and size of zinc sulfide nanoparticles ablated by ultrashort laser pulses

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The influence of microphysical processes in the synthesis of nanoparticles has been studiying. The effect of buffer gas and pressure on the cooling rate of ZnS nanoparticles obtained by ablation with ultrashort laser pulses is estimating. Elastic collisions of nanoparticles with buffer gas atoms are considering as the dominant process. The results of estimating the cooling time of ZnS nanoparticles with sizes 10^{-9}, 10^{-8}, $5 \cdot 10^{-8}$, and 10^{-7} m, depending on the buffer gas pressure, are presenting.

Keywords: Ablative synthesis of zinc sulfide nanoparticles, control of nanoparticle dispersion, femtosecond laser ablation.

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Laser ablation is one of the promising directions in the field of synthesis of nanoparticles with given properties [1–3]. Although a large number of studies focused on ablation synthesis have already been published, the processes governing the size of ablated particles in experiments with ultrashort laser pulses in gaseous media have not been investigated in sufficient detail. One important task is to identify and study the factors dominating after the ejection of a particle from the region of laser radiation. Microphysical processes are understood here as elastic collisions between zinc sulfide particles and buffer gas particles. The ablation conditions specify the end size of the nanoparticles, their dispersion, and the morphology of the nanoparticle surface. In the present study, we consider temperature conditions facilitating the process of aggregation of particles, which implies that they should coalesce before their surface cools. Control over thermal processes provides an opportunity to adjust the particle size distribution and the surface condition of particles. Literature data [4–6] suggest that the energy of photons in ablation with ultrashort laser pulses is transferred first to the electronic subsystem; owing to a short pulse duration coupled with a relatively high pulse energy, spallation in observed. Particles emitted from the material surface have a temperature comparable to the temperature of a plasma plume, which, according to literature data, is on the order of $3000-6000$ K [7–9]. In the process of dispersion, particles cool to a temperature at which aggregation is infeasible. We assume that this temperature is 800 K for a ZnS particle; according to [10], efficient diffusion is achieved at temperatures of $1100-1400$ K. Considered are the conditions of laser ablation under which repeated exposure of particles to laser radiation, plasma, and an erosion plume is excluded. This allows us to simplify the assessment significantly without compromising the correctness of the obtained result.

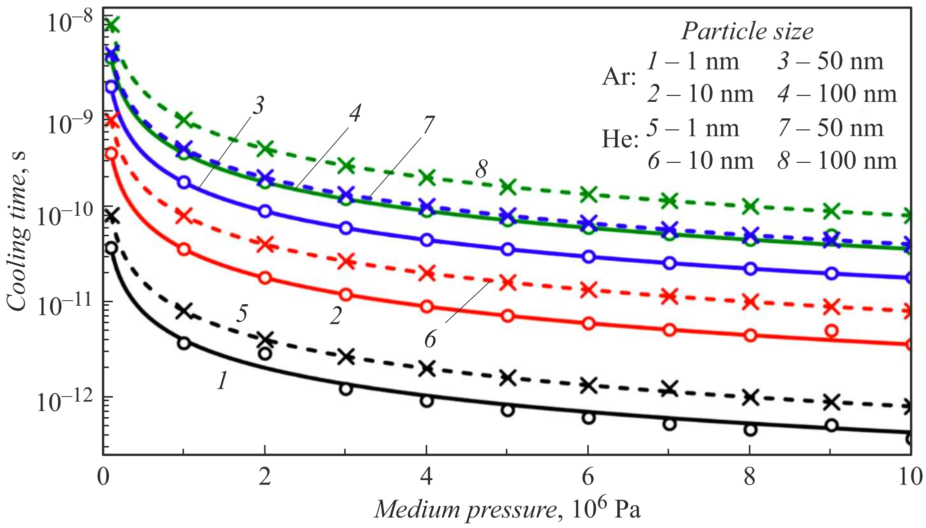
The presented assessment is relevant to the study of ablation of a zinc sulfide target by ultrashort laser pulses in a buffer gas (argon and helium) medium from the moment a particle leaves the laser irradiation region. The use of an inert gas (Ar or He) allows one to disregard the change in energy during the formation of new chemical bonds. Radiation with an energy of about 100 μJ, a pulse repetition rate of 10 kHz, and a pulse duration of 280 fs was used. The experimental setup and procedure were discussed in detail in [11]. The ZnS surface was processed in an inert gas (Ar, He) medium, and ablated particles left the laser beam propagation area without repeated exposure. The indicated process was stimulated by an electrostatic field. A 10-mm-thick ZnS material sample was used in the experiments.

Radiation energy losses by a particle and energy losses in collisions of a ZnS particle with buffer gas atoms (elastic and inelastic collisions) may be distinguished among the processes occurring after laser ablation in a buffer gas medium. The total energy loss of a particle in elastic collisions may be written as

$$Q = NE_{el}, \qquad (1)$$

where Q is the total energy loss of a particle, N is the number of elastic collisions, and E_{el} is the energy lost by a particle in a single elastic collision.

According to estimates, radiation losses are on the order of 10^{-19} J, which suggests that this loss process is not the dominant one. In view of this, only elastic collisions are included in relation (1). It was assumed that the initial temperature of particles corresponds to an average value of 3000 K, since plasma thermalization (establishment of equilibrium between ion and electron temperatures) is feasible at this temperature. It was taken into account in



Dependence of the time of ZnS particle cooling to 800 K in the course of elastic collisions on the buffer gas pressure.

calculations of the total time of nanoparticle cooling from 3000 K to the lower temperature limit of 800 K that Δt_1 depends on the buffer gas pressure and the mean free path of a nanoparticle decreases with increasing pressure. The average number of collisions of a nanoparticle may be calculated as

$$\tilde{n} = \frac{v}{\lambda}, \quad (2)$$

where $\tilde{n}$ is the average number of collisions of a nanoparticle within its mean free path, v is the average velocity of buffer gas atoms, and λ is the mean free path.

The total time spent on cooling is equal to

$$\Delta t = \Delta t_1 \tilde{n}, \quad (3)$$

where Δt is the total cooling time and Δt_1 is the time per a single collision.

Gas (argon and helium) was considered in calculations of the free path and energy losses due to elastic collisions. Estimates were obtained for particles with a size of 10^{-9}, 10^{-8}, $5 \cdot 10^{-8}$, and 10^{-7} m; the lower size limit was chosen in accordance with literature data [12,13]. If we assume that one of the particles is stationary (since the mass of a ZnS nanoparticle under the above conditions is much greater than the mass of a buffer gas atom), the energy losses due to elastic collisions are given by

$$E_{el} = m_1 m_2 v_1^2 / 2(m_1 + m_2), \quad (4)$$

where m_1 is the mass of a buffer gas atom, m_2 is the ZnS particle mass, and v_1 is the velocity of a buffer gas atom.

The upper pressure limit in calculations was set to 10^7 Pa, which corresponds to the performance capabilities of the equipment for experiments on laser synthesis of nanoparticles with adjustment of pressure in the vessel. The calculated dependence of the time of cooling of a ZnS particle to a temperature of 800 K in the course of elastic collisions on the buffer gas pressure is shown in the figure.

It is seen clearly that the temperature decrement depends on the particle size and the buffer gas pressure: the smaller a particle, the faster it cools. It is also evident that argon cooling is more efficient, which is attributable to the fact that helium atoms are lighter than argon ones. The obtained picosecond time scales are in good agreement with the results reported in [14]. The authors of this paper have examined the spatiotemporal dynamics of laser ablation and found that the conditions for synthesis of small primary nanoparticles are established within the range from $2 \cdot 10^{-11}$ to $2 \cdot 10^{-10}$ s. The subsequent growth and aggregation of nanoparticles within a plasma plume is the process of formation of a fraction of larger secondary nanoparticles, which is the key factor determining the resulting fractional composition of the obtained powder material. A higher buffer gas pressure level is conducive to particle energy loss. This is attributable to shortening of the free path of an ablated particle. An increase in buffer gas pressure translates into an increase in density of the medium in which the ablation products propagate, and a particle undergoes more collisions with atoms of the buffer gas. The data obtained during the evaluation are consistent with the results of an earlier experiment on synthesis of nanoparticles under the influence of ultrashort laser radiation and varying pressure levels [11].

The evaluation of cooling rate of a nanoparticle as a function of buffer gas pressure is of interest in various fields of physics (in particular, in ablation laser synthesis of nanomaterials). We believe that the bimodal distribution of nanoparticle sizes characteristic of ablation by subpicosecond laser pulses under atmospheric conditions depends directly on the rate of cooling of ablation products. The fraction of large particles is the result of aggregation of ablation products. One may alter the initial temperature of formed nanoparticles and control the rate of their cooling by varying the laser radiation power density and changing the buffer gas pressure. Data on the dependence of the cooling time of ablation products on the buffer gas pressure should allow one to synthesize particles with predetermined sizes by establishing such conditions that suppress the processes of coagulation of nanomaterials. This is especially important in fields where spherical nanoparticles of a given size (with a predetermined range of dimensions) are used.

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Conflict of interest

The authors declare that they have no conflict of interest.

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