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Influence of cooling rate on the size of zinc sulphide nanoparticles during laser ablation synthesis

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The paper examines the dependence of the sizes of the resulting nanoparticles on the cooling rate of the products of laser ablation of zinc sulfide. The influence of the buffer gas pressure parameter on the dynamics of cooling of ablation products is considered. The results of an assessment of the cooling of nanoparticles due to thermal radiation and collisions with a buffer gas are presenting. The results were obtaining based on molecular dynamics methods.

Keywords: ablative synthesis of nanoparticles, control of nanoparticle dispersion.

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1. Introduction

The laser ablative synthesis of nanoparticles is an effective method to produce nanomaterials used both in laboratory and in industry [1–3]. This method ensures nanoparticles synthesis of a wide range of materials. Change of exposure parameters, such as pressure of buffer gas, energy per pulse, mode of lase exposure, ensures accurate setting of the synthesis processes, change of chemical, phase composition, production of combined nanoparticles [4,5]. During synthesis of the nanoparticles produced by the laser ablation, we shall consider effect of buffer gas pressure, as it directly affects the characteristics of the ablation products and dynamics of the synthesis process [6].

2. Samples and study method

The conditions of the laser ablative synthesis are considered when using femtosecond laser pulses 280 fs with energy $\sim 100\,\mu$J per pulse, with pulse repetition rate 10 kHz, and laser radiation wavelength 1030 nm. As target the zinc sulfide was used, sample is a bar with size $30 \times 30 \times 30$ mm. The ablated nanoparticles were gathered using the electric filer. The particle size was measured using a scanning-electron microscope; for one sample, at least 10 images were used, on which the outline of the particles was clearly visible; as a result of the measurements the average size from each sample was calculated (Figure 1). As a result of the laser radiation absorption by the material surface,as per data [7], the set of processes of energy exchange is complex, without a single interpretation issue. In paper we directly consider the material ejected from the surface. We consider that the ablated particles were not subjected to repeated exposure of the laser beam, cooling was performed by interaction with the buffer gas, pressure increasing stimulates the ablated materials cooling. The buffer gas density increasing facilitates the probability decreasing of aggregates formation. Such evaluation ensures understanding of some microphysical processes and kinetics during the nanoparticles aggregation.

Upon pressure increasing of the buffer gas the density of atmosphere, where the material is treated, increases this results in increase in concentration of particles of the argon buffer gas. As a result, the mean free path of ablated particles „flying“ from the sample surface decreases due to multiple collisions with gas atoms, at that transferring part of their energy. Such hypothesis can be confirmed based on calculations of the energy losses depending on pressure using the method of molecular dynamics [8].

Based on heat-balance equation we can calculate general energy losses Q of the particle until reaching some limit temperature when the particle can not aggregate. According to papers [9–11] we consider initial temperature o particles to be ~ 4000 K. The lower limit o particle temperature corresponds to temperature, at which the development of diffusion and aggregation processes is impossible, let's this

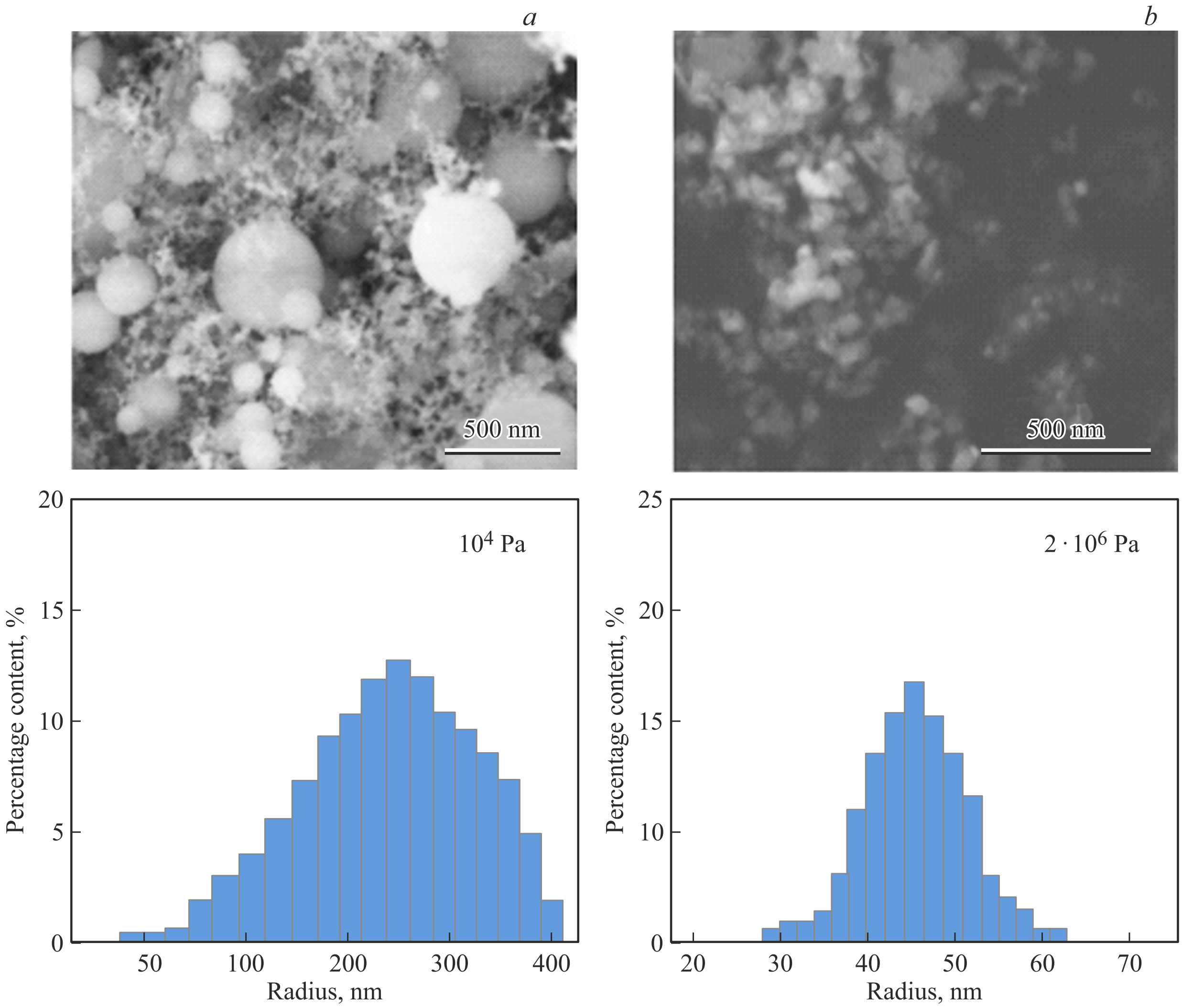

Figure 1. Histograms of distribution by size of ZnS particles and corresponding SEM images. *a* — particles synthesized at argon pressure of 10^4 Pa, *b* — at argon pressure of $2 \cdot 10^6$ Pa.

temperature will be 500 K:

$$Q = cm\Delta T. \qquad (1)$$

So, general energy losses of the nanoparticle during cooling to 500 K will be $3.52 \cdot 10^{-15}$ J. To calculate the losses for collisions the mean free path of the particle shall be calculated. Let's use formula or mean free path calculation depending on pressure [12]:

$$\tilde{\lambda} = \frac{kT}{\sqrt{2}\pi d^2 p}, \qquad (2)$$

where d — dimeter of ZnS particle.

Based on data obtained we can calculate number of collisions if argon atoms. Let's use known formula for calculation of mean speed of atom substituting value of argon atom mass equal to $6.63 \cdot 10^{-26}$ kg:

$$\tilde{v} = \sqrt{\frac{8kT_{\text{h}}}{\pi m}}. \qquad (3)$$

Let's calculate energy loss ΔW_{elas} at elastic collision in case if one of particles is fixed, i.e. $\nu_2 = 0$:

$$\Delta W_{\text{elas}} = \frac{m_2}{m_1 + m_2} \cdot \frac{m_1 \cdot \nu_1^2}{2}. \qquad (4)$$

Apart elastic collisions in this problem we shall consider also inelastic collisions, as during collision of particle ZnS with atom Ar the energy transfer occurs, it further is converted into internal energy. During energy transfer to Ar atom the transition rom the ground state into the excited state [13] is possible, or this process it is necessary to transfer to Ar atom the energy equal to $1.85 \cdot 10^{-18}$ J [14]. So, energy lost by ZnS particle during 1 collision with Ar tom is

$$\Delta W_{\text{inelas}} = \frac{m_2}{m_1 + m_2} \Delta E_{12} = 1.8499 \cdot 10^{-18}\ \text{J}. \qquad (5)$$

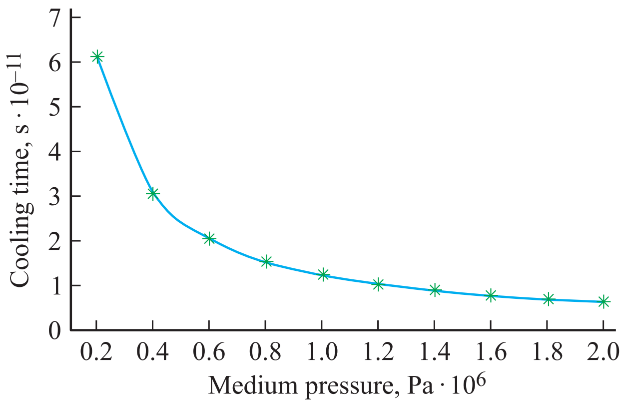

Figure 2. Dependences of mean time of particle cooling to 500 K on buffer gas pressure.

Radiation losses E_{rad} will be calculated as per relationship

$$E_{\text{rad}} = T_0 cm \cdot \left(\frac{1}{\sqrt[3]{\frac{3\sigma S T_0^3}{cm} t_x + 1}} - 1 \right). \qquad (6)$$

3. Results and discussion

Considering the previously obtained data on average number of collisions per 1 s depending on buffer gas pressure, we can obtain time dependence when the particle losses energy during collisions at set pressure of buffer gas (Figure 2).

The made evaluation shows that the higher the buffer gas pressure is the quicker particle will loss energy, which excludes its size increasing due to aggregation with other particles. As a result of the increase in argon pressure, the density of the atmosphere also increases, which leads to decrease in the mean free path of particles; at a shorter distance the particle encounters a greater number of atoms of the buffer gas Ar than at lower pressure. The data obtained are confirmed by the previous experiment on synthesis of titanium nanoparticles in atmosphere of buffer gas argon at different pressures. With pressure increasing the size of synthesized particles decreases. At the buffer gas pressure 630 Pa the average size of particles is 82 nm, at pressure 106 Pa the average size of particles is 74 nm, at pressure $2 \cdot 10^6$ Pa the average size of particles decreased to 47 nm [6].

4. Conclusion

Control of cooling rate of nanoparticles during laser ablative treatment due to pressure change of the inert gas ensures control of size range and particles dispersion. Considering rate of spreading of ablated particles, at permanent initial energy, the increase in cooling rate leads to decrease in ability of aggregation into larger particles. The made evaluations clearly demonstrate the influence of the temperature of ablated particles on the pressure parameter of the buffer gas. This conclusion is confirmed by the made measurements of size of ZnS particles synthesized by femtosecond laser ablation, at argon pressure 1 bar there is wide scattering particles by size, average size of particles is in range of 200–300 nm, at pressure 20 bar the particles scattering by size decreases, the average size is 47 nm.

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Conflict of interest

The authors declare that they have no conflict of interest.

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