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Laser Irradiation of Gd–Si and Gd–Si–Ge Colloid Mixtures for the Fabrication of Compound Nanoparticles

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Binary (Gd_5Si_4, GdSi) and ternary ($Gd_5Si_2Ge_2$) compound nanoparticles (NPs) were prepared by laser irradiation of a mixture of colloidal solutions containing NPs of the relevant elements. It is assumed that the compound NPs are formed by heating, co-melting, and chemical interactions in the alloyed droplets. The blackbody-like radiation of the heated NPs was used for temperature control of the NP-preparation process. The obtained results demonstrate that laser irradiation of colloidal NPs provides unique possibilities not only for the synthesis of compound NPs but also for control of their phase composition and size. The synthesized Gd-based compound NPs exhibited magnetic transition at an ordering temperature, T_C, in the range of 310–320 K. Thus, the magnetic properties of the synthesized particles confirm their potential for biomedical applications, in particular, for magnetic hyperthermia treatment.

1. Introduction

In the last decade, laser-induced modification (LIM) of nanoparticles (NPs) in solution gained an increased interest and it is now referred as one of the major issues in the field of laser-matter interactions aiming the targeted changes of the NPs properties. One of the characteristic features of the LIM technique is a very rapid space-selective heating with subsequent fast cooling that can result in a change of the NPs size through the fragmentation and aggregation processes, their composition and inner structure through the phase transitions, and crystal structure through the defects removal and doping.[1–4] The results of laser treatment are dependent on the exposure conditions (laser fluence, laser pulse duration, exposure time, etc.), as well as on the kinetics of relaxation processes in the surrounding medium and the properties of the material constituting NPs (specific heat, density, absorption efficiency, etc.). Important application of LIM technique is production of submicrometer spherical particles of various materials, such as metals (Au,[5] Ag[6]), oxides (ZnO,[7] TiO_2[8]), semiconductors (Si,[9] Ge[10]) and carbides like B_4C.[11] In these LIM experiments, initial NPs dispersed in a liquid are irradiated by a pulsed laser with a moderate fluence of about 50–200 mJ pulse^{-1} cm^{-2}, that results in melting and fusion of irradiated particles and subsequent submicrometer-sized spherical particle formation after fast cooling.

One of the important novel applications of LIM is related to the alloying and multielement particles formation upon laser irradiation process. For example, experimental results are presented on laser alloying of Co nanorods[12] with Al spherical NPs by laser exposure of their mixture in ethanol. The results are discussed from the viewpoint of interaction of molten NPs inside the cavitation bubble filled with vapor of liquid.[13,14] Another example of novel LIM application is the formation of microring structures containing gold NPs which have tunable plasmonic properties and show the potential for the plasmonic sensors development.[15] LIM of thin gold ultra-thin films to NPs with controllable size and area density after nanosecond-laser irradiation has been investigated in.[16,17]

To explain the mechanism and to predict the result of LIM of NPs in solution, several theoretical models were proposed. Most of them are based on the evaluation of the balance between the heat absorbed by the metal nanoparticle and removed due to the heat losses.[18–22] For example, the processes of heating and melting of single Au NP in water and NP complexes with polymers were theoretically studied, and the conditions for the significant increase in the temperature of the surrounding material were estimated.[20] Pustovalov et al.[18] developed a theoretical model for heating of an absorbing nanoparticle in a tissue by a laser pulse that can be used for the description of the nanoparticle temperature rise that determines the final result of the laser pulse action. In the other works, the influence of NPs shape (spherical, ellipsoidal) and temperature dependences of the optical and thermo-physical parameters of NPs and surrounding media on the result of laser modification have been studied.[18,22]

As the result of laser modification of NPs is mostly determined by the temperature that is reached during the

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irradiation, particles temperature control is essential for the correct interpretation of the observed phenomena. The possible way to determine the temperature of the heated NPs is based on the detailed analysis of the heated particles emission spectra.[23–25]

It should be noted that in the studies on the LIM of NPs in mixtures of colloidal solutions, the main attention has been paid to the alloyed NPs formation and evolution of their microstructure, but to the best of our knowledge, the chemical interaction between NPs and the formation of the compound particles are much less studied. In our previous work,[26] we have shown that binary gadolinium silicide compound NPs could be spontaneously formed due to the aggregation and coalescence as the result of the mixing of their colloidal solutions. However, to enhance the production efficiency and to provide a possibility of the controlled synthesis, additional laser processing of a mixture of gadolinium and silicon colloids is expected to be more effective.

In this paper, we present the results of the experiments on laser irradiation of the mixture of Gd and Si colloids for the synthesis of gadolinium silicide NPs. In addition, we have expanded the LIM method for synthesis of ternary $Gd_5Si_2Ge_2$ NPs by laser irradiation of the ternary mixture. To control laser heating of particles, radiation emitted from the hot NPs was measured and analyzed using the blackbody-like approximation.

Nanoscale compounds of gadolinium, due to the unique combination of high magnetization and superparamagnetic behavior, are promising materials for a wide range of technological and medical applications. Their use as therapeutic agents in drug delivery, contrast agents in magnetic resonance imaging (MRI) and magnetic resonance angiography (MRA) as well as application of these magnetic particles in the hyperthermia treatment of tumors are good examples.[27]

To prepare Gd compound NPs with sizes and phase composition adjusted for the given application, several experimental tasks must be accomplished. The particles modification thresholds, mean size and structure dependencies on laser fluence and laser pulse duration should be established to be able to predict the optimum laser parameters for selected nanoparticle size and structure modification. The conclusions on the prevailing mechanism of NPs transformations in every case are made based on the study of their morphology and inner structure.

2. Results and Discussion

2.1 Nanosecond Laser Irradiation of a Gd-Si Mixture

2.1.1 Morphology and Structure

The initial Gd and Si NPs separately prepared by laser ablation in ethanol have nearly spherical shape with diameters of 12 nm for Gd and 7 nm for Si (Figure 2 b,c). As can be concluded from the TEM analysis (Figure 1), the formation of gadolinium silicide starts in the mixture of colloids due to the high surface energy and defect structure of NPs prepared by the laser ablation in liquids (Figure 1b). Mixing the particles in one solution resulted in the formation of several types of NPs: in addition to the small spherical particles (A), that mostly form aggregates, large nearly-spherical particles with the diameter more than 70 nm (B) as well as some hollow NPs (C) were formed. The SAED patterns analysis of the mixture samples proves that NPs are mostly polycrystalline as well-defined rings are seen on the patterns (see Figure 2b). However, the compound gadolinium silicide phases were found in the large near-spherical particles only, where compound Gd_5Si_4 and GdSi phases formed along with the cubic Si and Gd and hexagonal graphite phases. The formation of the binary Gd_5Si_4 compound was proved by the presence of the reflections from (112), (230), (231), (114), (151), (060), (242), (104), (163) and (343) planes of the orthorhombic Gd_5Si_4 phase (space group Pnma, No. 62).[29] The lattice parameters calculated using the results of electronic diffraction were found to be $a=8.18$ Å, $b=12.78$ Å, and $c=7.71$ Å that proves rather strong lattice distortion in the NPs compared to the bulk compound.[29] It should be noted that a trace amount of carbon or gadolinium carbide phases can also be formed as the result of the partial decomposition of ethanol during the laser ablation and consequent reaction of fragments with gadolinium.

Nanosecond laser irradiation of the colloidal solution mixture results in a further change of the NPs morphology and their phase composition. The particles size growth after laser irradiation of the colloid mixture can be the evidence of their co-melting after the initially small NPs aggregation that can result in the compound NPs formation. As a rule, the lattice of the NPs produced by laser ablation is distorted, so interdiffusion of the components is possible. It was found that the laser modification result depends on the laser fluence. TEM images shown in Figure 1 reveal the increase in the NPs size after the laser irradiation both with fluences 0.23 J/cm^2 and 0.40 J/cm^2. However, the composition of NPs irradiated with different fluences is not the same. Laser treatment with fluence 0.40 mJ/cm^2 results in the formation of orthorhombic GdSi phase while the major phase that constitutes NPs irradiated with fluence 0.23 J/cm^2 is Gd_5Si_4 that is proved by the presence of the reflections from (141), (231), (252), (401), (134), (431), (144) and (343) planes of Gd_5Si_4 in the SAED pattern.[29] The lattice parameters calculated using the results of electronic diffraction were found to be $a=7.51$ Å, $b=13.99$ Å, and $c=7.77$ Å that reveals the significant crystallinity improvement after the laser treatment. Table 1 summarizes the Gd_5Si_4 lattice parameters

Table 1. Lattice parameters [Å] of the NPs in the mixture before and after laser irradiation.

Lattice parameter	Samples [Å] Bulk	Mixture	ns-Laser irradiation (0.23 J/cm^2)	ps-Laser irradiation (1 W)
a	7.49	8.18	7.51	7.44
b	14.75	12.88	13.99	14.74
c	7.75	7.71	7.77	7.75

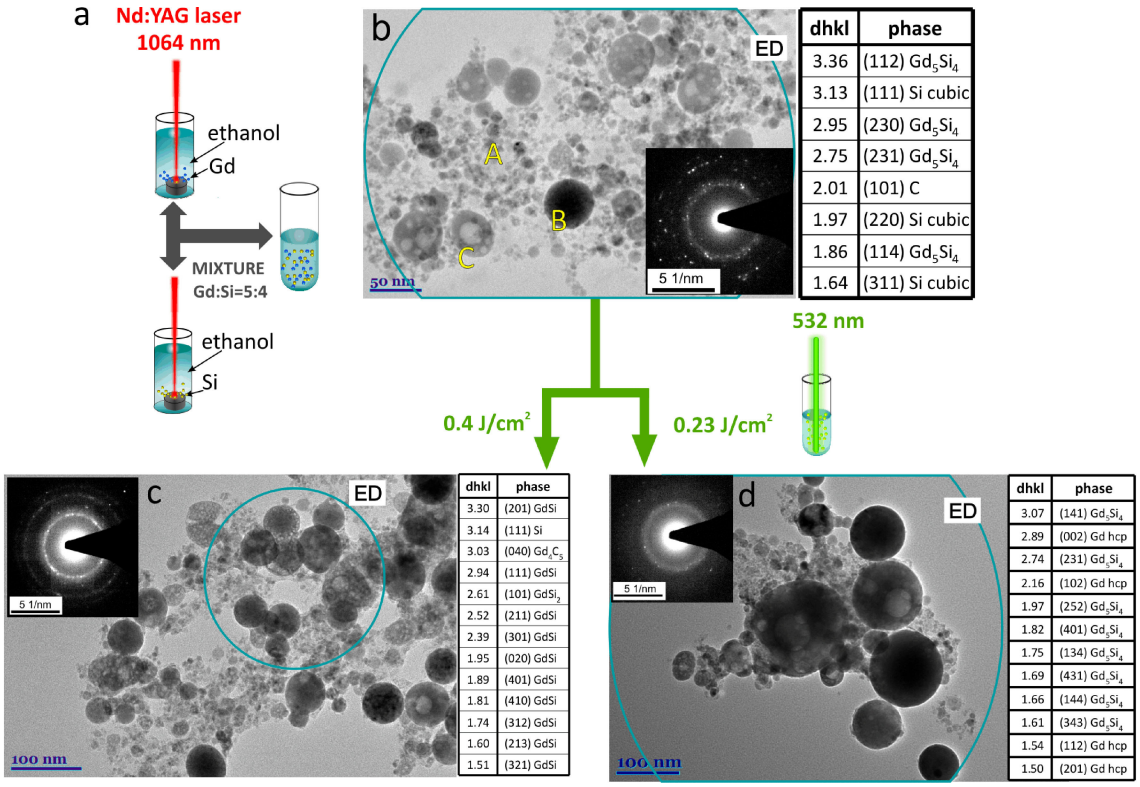

Figure 1. Preparation of compound NPs by nanosecond laser irradiation of Gd and Si NPs mixture: (a) schematic diagram of the experimental procedure; b, c, d – TEM images, SAED patterns and their analysis (insets) of NPs formed in the Gd–Si mixture before (b), and after laser irradiation with fluences of 0.4 J/cm^2 (c) and 0.23 J/cm^2 (d), respectively. ED denotes the area selected for SAED analysis. The indexing of the SAED patterns reveals the formation of compound phase in the mixture of NPs, additional laser treatment allows to vary the NPs composition with the preferential formation of GdSi after laser irradiation with 0.4 J/cm^2 and Gd_5Si_4 – with 0.23 J/cm^2 laser fluence.

values for the NPs before and after ns and ps (see the discussion below) laser treatment with the bulk values taken from[29] presented for comparison.

2.1.2 Temperature Evaluation of Laser-heated NPs

The major effect leading to compound NPs formation under laser irradiation with pulses of nanosecond duration is heating of particles and their further interaction in the liquid droplets. In this case, the pulse duration is long enough for both electron-electron and electron-phonon coupling to occur; therefore, the major parameter determining the processes in the particles is the maximal temperature that is reached under the laser irradiation. That implies the necessity of the experimental techniques development for the temperature evaluation during laser irradiation allowing the control over the composite NPs synthesis procedure.

Analysis of the emission spectra of the laser heated particles was performed to evaluate their temperature. In this method, the emission of the heated particles is assumed to be of the black body type and can be described by the Planck's law:[23–25]

$$I = \frac{hc^2}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1} \quad (1)$$

where I denotes the emission intensity in the $(\lambda, \lambda+\Delta\lambda)$ spectral region, λ is the wavelength, T is the absolute temperature, c is the speed of light, h is the Planck constant, k_B is the Boltzmann constant.

Taking into account the emissivity of NPs (ε) the expression (1) can be written as:

$$I \propto \varepsilon(r,\lambda)\frac{1}{\lambda^5}\frac{1}{\exp\left(\frac{hc}{\lambda k_B T}\right) - 1} \quad (2)$$

According to the Mie theory, the emissivity of the small nanoparticle under condition $2\pi r/\lambda \ll 1$ is:[30]

$$\varepsilon = \frac{8\pi n_m r}{\lambda}\mathrm{Im}\left(\frac{m^2-1}{m^2+2}\right) \quad (3)$$

where n_m is the refraction index of the surrounding medium, $m = n_p/n_m$, where n_p is the refraction index of the particle material and r is the particle radius, m is the complex refractive index, Im is the imaginary part of the expression in brackets.

The emission spectra of the laser irradiated Gd and Si particles are presented in Figure 2.

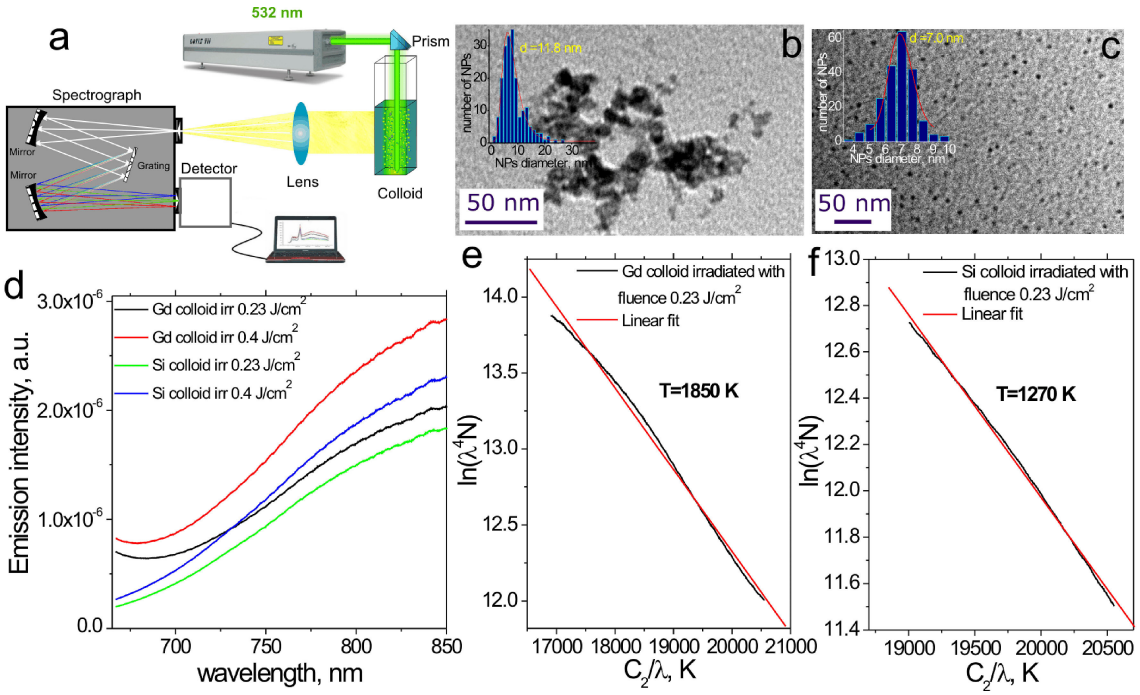

Figure 2. The measurement of the thermal emission of the NPs in solution: (a) the scheme of the setup used for registration of the thermal emission spectra; b, c – TEM images of the corresponding Gd (b) and Si (c) NPs prepared by laser ablation in ethanol, respectively, the insets show the size distributions of the prepared NPs with the average diameters estimated from the lognormal distribution – 11.8 nm for Gd and 7.0 nm for Si; d – thermal emission spectra of ns laser irradiated Gd and Si NPs in ethanol with fluences of 0.23 and 0.4 J/cm^2; e, f – plots $ln(\lambda^4 N)$ vs C_2/λ for the emission spectra of heated Gd (e) and Si (f) NPs under the laser irradiation with fluence of 0.23 J/cm^2. The estimated temperature was found to be 1850 K for Gd and 1270 K for Si NPs.

By correcting the measured emission spectra of NPs and fitting them by the theoretical curves (2), it was possible to estimate the temperature of the particles in solution excited by the laser pulses. If $\exp[hc/\lambda k_B T] \gg 1$, the expression (2) for the photon number N in the $(\lambda, \lambda+\Delta\lambda)$ spectral region (taking into account that the CCD detector counts the photon number) can be written as:[24]

$$\ln(\varepsilon C_1/hc) - \frac{C_2}{\lambda T} = \ln(\lambda^4 N) \quad (4)$$

where $C_1 = hc^2 = 3.742 \cdot 10^{16}$ W nm^4/cm^2, $C_2 = hc/k_B = 14388$ nm K. This expression graphically built in the coordinate system with $x = C_2/\lambda$ and $y = ln(\lambda^4 N)$ can be approximated by a straight line whose slope is determined by the temperature (see Figure 2).

The resulting temperatures for the Gd and Si NPs irradiated with a fluence of 0.23 J/cm^2 were found to be about 1850 K and 1270 K, respectively, that is higher than the melting temperature of Gd (1586 K) but below the melting point of bulk Si (1688 K). However, it should be taken into account that due to the size effects melting point of NPs is generally lower than that of bulk material.[31] Moreover, the formation enthalpies of all the solid Gd silicides phases and their enthalpies of mixing in the liquid state are negative, that may also favour the reaction between the Gd and Si atoms in the liquid droplets.

The heat diffusion model was used to verify the determined temperature. It is assumed that the incident laser radiation is absorbed by the particle on the first stage while the solvent is transparent at the laser wavelength. Generally, these models are based on the heat transfer equation between the particle and the surrounding medium:[18,19]

$$\rho c V \frac{dT}{dt} = I(t) K_{abs} S - 4 J_{loss} S \quad (5)$$

with the initial condition

$$T(t=0) = T_0 \quad (6)$$

where T is the temperature reached under laser irradiation of a particle with the radius r by laser radiation with the intensity $I(t)$, ρ, c and S are the density, heat capacity and surface area of the particle, $K_{abs}(r,\lambda)$ is the absorption efficiency factor of incident laser energy by a particle of radius r,[30] J_{loss} is the energy flux density from the heated particle due to the heat loss mechanisms, such as thermal conductivity, thermal emission, phase transitions, chemical interactions, etc.

The quasi-stationary temperature distribution in the surrounding medium is reached only if the time required for heat exchange between a nanoparticle and surrounding medium exceeds the characteristic time t_T that depends on the particle radius r and thermal diffusivity coefficient of the surrounding medium χ: $t_T \sim r^2/4\chi$. For particles with a diameter of 5 nm dispersed in ethanol with thermal diffusivity $8.94 \cdot 10^{-8}$ m^2/s[32] irradiated by nanosecond pulses, the t_T value was found to be $7.0 \cdot 10^{-11}$ s, that is much shorter than the pulse duration (10^{-8} s). It is noteworthy that the resulting temperatures are high enough to evaporate the liquid ethanol surrounding the

particle and thus the particle after the action of the laser pulse is surrounded by an ethanol vapor bubble. In this case, the thermal diffusivity of ethanol vapor is $\chi = 1.67 \cdot 10^{-9}$ m^2/s[33] and characteristic time $t_T = 3.7 \times 10^{-9}$ s is still less than the pulse duration. Therefore, in both cases, the quasi-stationary conditions for heat exchange between a particle and surrounding liquid can be supposed.

The maximal temperature reached at the end of the laser pulse can be estimated based on the evaluation of heat absorbed by the particle (Q_{abs}) and of the heat losses (Q_{loss}) due to the convection, emission, phase transitions and chemical reactions.

$$\Delta E = Q_{abs} - Q_{loss} \tag{7}$$

where ΔE – change of the particle thermal energy during the heating process:

$$\Delta E = E_T - E_{T0} = \frac{\rho_T c_T V}{Mr} T - \frac{\rho_0 c_0 V}{Mr} T_0 \tag{8}$$

where ρ_T and ρ_0 are the density, c_T and c_0 are the specific heat of the particles material at final and initial temperatures, V is the particle volume. The temperature dependence of the Gd specific heat was interpolated by the function $c_T = a - bT + cT^2$ with a, b and c parameters taken from.[34] The temperature dependence of the Si specific heat was taken from.[35] Besides, it should be taken into account that gadolinium undergoes a phase change from alpha to beta phase at 1508 K and melts at 1586 K. Si melting temperature is known to be 1688 K. Therefore, the enthalpies of the corresponding phase transitions were taken into account as well.

It should be noted that generally, the density of a material is temperature dependent, but the change is insignificant in the absence of such mass transfer processes as evaporation, and thus it can be assumed that the density does not change during the nanoparticle heating.

The absorbed laser energy can be evaluated according to the equation:

$$Q_{abs} = \pi r^2 \int_0^{t_p} I(t) K_{abs} dt = \pi r^2 I t_p K_{abs} \tag{9}$$

where I is the laser fluence, t_p is the laser pulse duration, r is the nanoparticle radius.

Theoretically, K_{abs} can be estimated using Mie theory:[30]

$$K_{abs} = -\frac{8\pi r}{\lambda} \mathrm{Im}\left[\frac{m^2 - 1}{m^2 + 2}\right] \tag{10}$$

where $m = n - ik$ is the complex refractive index of NPs, n is the refractive index, k is the extinction coefficient of the particle material.

Because of the lack of the reliable literature data on the temperature-dependent optical properties of Gd and Si, K_{abs} calculation was performed based on the analysis of the absorption spectra of the corresponding colloids in ethanol. For this, the absorption cross-section was estimated using the relation $\sigma_{abs} = \frac{A}{C \cdot l \cdot \lg e}$, where A is the absorbance at 532 nm, C is the concentration of the particles in solution, l is the optical path, that was 1 cm in our experiment.

The particles concentration in the solution was estimated based on the measurement of the corresponding Gd and Si content by inductively coupled plasma optical emission spectroscopy calibrated by the standard water solutions.[36] The estimated content of the Gd and Si atoms in solution was found to be 0.38 mM for Gd and 0.53 mM for Si. Taking into account the average diameters of the NPs, the concentrations of the Gd and Si NPs were evaluated to be $8.37 \cdot 10^{12}$ cm^{-3} and $3.55 \cdot 10^{13}$ cm^{-3}, respectively. The K_{abs} values were calculated using the estimated absorption cross-sections: $K_{abs} = \frac{\sigma_{abs}}{\pi r^2}$ and were found to be 0.068 and 0.035 for Gd and Si NPs, respectively.

Supposing that the main mechanisms of the heat dissipation are heat conduction and melting of the particles for the corresponding quantities of energies the following expressions can be written:

$$Q_c = 4\pi r^2 \int_0^{t_p} J_c dt \tag{11}$$

$$Q_m = \rho V L_m \tag{12}$$

where $J_c = -\left(k(T)\frac{dT}{dr}\right)_{sp}$ is the heat flux from the heated NP due to the heat conduction, L_m is the molar heat of fusion, $k(T)$ is the coefficient of thermal conductivity of the surrounding liquid. It should be noted that in the temperature range under study, the radiative heat losses through the thermal emission are much less than the losses through other routes and, therefore, can be neglected. Thus, substituting the corresponding energy values into equation (7) the resulting temperature reached at the end of a laser pulse was calculated to be around 1900 K and 1000 K for Gd and Si, respectively, irradiated with laser fluence of 0.23 J/cm^2 as well as 2500 K and 2400 K for Gd and Si NPs irradiated with laser fluence of 0.4 J/cm^2. It should be noted rather good agreement between the NPs temperatures evaluated from the thermal emission and heat diffusion model for Gd and some discrepancy for Si NPs. The observed disagreement can be attributed to the impact of luminescence on the emission of the 532 nm irradiated Si NPs as well as non-sufficient accuracy of the literature data for the optical constants applicable to NPs.

In the mixed colloid, particles diffuse and collide with each other, which can lead to reactions and formation of the compound particles. In this case, the heat exchange takes place between the particles depending on the magnitude of the resulting temperature.

Thus, upon laser heating of the mixture of Gd and Si colloids, compound NPs can be formed as the result of the collisions between initial NPs followed by the heat transfer

between NPs, diffusion processes and chemical reactions in the formed aggregates. It should be noted that under the proper selection of the laser exposure conditions (power, wavelength, frequency, cooling mode, etc.), it is possible to achieve the dominant formation of one or another single-phase product, which is of interest for practical applications.

2.2 Picosecond Laser Irradiation of a Gd-Si Mixture

To study the effect of pulse width on the properties of the NPs formed, the results of the Gd–Si mixture irradiation with ns- and ps-laser pulses were compared. The results obtained by irradiation with the second harmonic of the picosecond Nd:YVO_4 laser (wavelength 532 nm, pulse duration 10 ps) with the power ranging from 1 to 5.3 W reveal similar laser-induced effects as can be concluded from Figures 3 and 4. Laser irradiation generally results in the initiation of agglomeration of small Gd and Si particles into large spherical ones; the process of the LIM was more effective by using the second harmonic radiation as compared to the fundamental wavelength because of spectral selectivity of the light absorption by particles.

As in the case of the ns-laser treatment, laser fluence is an essential factor determining the major processes occurring under ps-laser irradiation and, consequently, the composition and structure of the final NPs.

Figures 3 and 4 illustrate the differences in the inner structure of the particles obtained by laser irradiation with the power of 1 W and 4.7 W. While after the laser treatment with a lower fluence the particles are mainly composed of Gd_5Si_4 orthorhombic phase with the remaining initial hexagonal Gd and cubic Si phases, after the laser treatment with a higher power, separated Gd and Si islands were present along with the mixed regions as it is evident from EDX and SAED analysis.

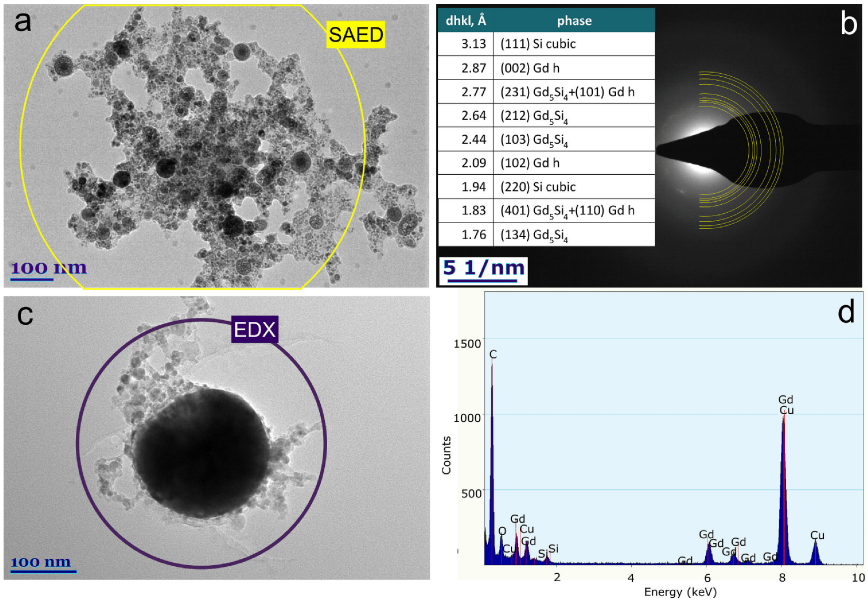

Figure 3. The analysis of composition and structure of Gd and Si NPs mixture modified with the picosecond Nd:YVO_4 laser radiation with the average laser power of 1 W. (a) TEM image with the area used for SAED analysis indicated; (b) SAED analysis of the corresponding area, the inset shows the result of the rings indexing, proving the formation of orthorhombic Gd_5Si_4 phase along with the cubic Si and hexagonal Gd phases; (c) the TEM image of the single large particle used for EDX analysis; (d) EDX spectrum of the large particle shown in Figure 3c, the observation of both Gd and Si lines can be the evidence of compound NPs formation.

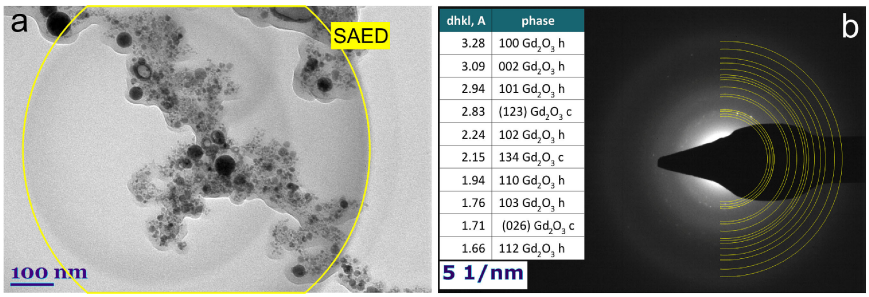

Figure 4. The NPs formed by Gd and Si NPs mixture laser modification by the picosecond Nd:YAG laser radiation with average laser power of 4.7 W. (a) TEM image; (b) SAED analysis of the area indicated in Figure 4a, the inset table with the results of rings indexing shows the preferential oxidation of the constituent NPs under laser irradiation with high power.

Herewith, the Gd-containing islands were mainly composed of Gd_2O_3 of the cubic and hexagonal structure.

Formation of the Gd_5Si_4 phase by the 1 W ps-laser irradiation was proved by the observation of the reflections from the (231), (212), (103), (401) and (134) planes in the SAED pattern (Figure 3b), and these results allow to estimate the lattice parameters of the obtained silicide structure as a = 7.44 Å, b = 14.74 Å, and c = 7.75 Å. That is close to the literature data and reveals much more ordered crystal structure after laser irradiation with the ps-laser pulses than for ns-laser case (see Table 1).

Comparing the results of LIM of Gd–Si mixture after its irradiation with the nanosecond and picosecond laser pulses it should be noted that the difference between two excitation regimes consists in shifting the power regime for melting and fragmentation to the lower laser power density for the picosecond excitation. These results are consistent with other studies[37,38] comparing the thresholds for melting of Au NPs with nanosecond and femtosecond or picosecond laser pulses and found that higher laser powers must be used for nanosecond excitation to induce NPs melting because of heat dissipation to the surroundings. In our experiments in case of the nanosecond excitation, formation of compound NPs occurs at laser energies of 50–60 mJ/pulse, while in the case of the 10 ps laser irradiation at the lower energies (10–50 μJ/pulse). Note that the duration of both laser pulses is much longer than the characteristic time of the electron-phonon (e-ph) coupling process which takes a few picoseconds. After the electron gas and lattice (phonons) have reached equilibrium, the absorbed energy is dissipated into the surroundings. Depending on the particle size the heat dissipation occurs on a 100–200 ps time scale,[39,40] which is much shorter than the nanosecond excitation pulse and much longer than the duration of the picosecond pulse. Due to the dissipation of the absorbed energy to the solvent during the nanosecond laser pulse, the particle temperature reached by nanosecond excitation is expected to be lower than that achieved by the picosecond excitation for equal pulse energies.

2.3 Laser Treatment of a Ternary Gd–Si–Ge Colloid Mixture

The prepared gadolinium silicide NPs can be promising materials for biomedical applications as MRI contrast agents, therapeutic agents in drug delivery and hyperthermia treatment. The role of Gd alloys and compounds in magnetic resonance imaging is already well established, and they are widely investigated in this regard.[27] As for hyperthermia treatment, the Gd silicide NPs can be proposed as potential candidates,[41,42] however, for the self-regulated variant of hyperthermia, their Curie temperatures (T_C = 340 K for Gd_5Si_4) lie somewhat higher the required therapeutic range even for very small sized particles. The magnetic hyperthermia method is based on the tissue heating by the application of the magnetic field to the magnetic nanomaterials introduced in the tissue and acting as heat sources. Therefore, for the self-controlled non-invasive magnetic hyperthermia treatment the superparamagnetic NPs with the magnetic ordering temperature (Curie temperature) in the range of 42–45 °C are required for the temperature control switch during the treatment to maintain a constant temperature in the tumor region.

Magnetic properties of Gd_5Si_4 NPs can be modified by replacing Si with Ge to form $Gd_5(Si_{1-x}Ge_x)_4$ compounds with $0 \leq x \leq 0.35$.[43] The ternary gadolinium compounds appear to be extremely attractive for self-controlled hyperthermia because they have a large saturation magnetization and their Curie temperature can be tuned in the range of 315–318 K by varying the composition.

As our experiments showed, the developed approach for fabrication of Gd silicides NPs based on laser irradiation of colloidal mixture can be expanded for a preparation of more complicated compounds, for example ternary Gd germanosilicide compounds.

For a ternary compound manufacturing, Gd, Si and Ge colloids were prepared separately by laser ablation of the corresponding targets placed in the cell filled with ethanol, and after that they were mixed in the following order Gd←Si←Ge taking the components in the proportion corresponding to the atomic ratio Gd:Si:Ge = 5:2:2. After that, the mixture was irradiated by ns-laser pulses of the second harmonic of the Nd^{3+}:YAG laser (wavelength 532 nm, pulse duration 10 ns, fluence 0.23 J/cm^2, 10 Hz, 30 min). The initial Gd, Si and Ge NPs separately prepared by laser ablation in ethanol have nearly spherical shape with diameters of 12 nm for Gd, 7 nm for Si and 7.2 nm for Ge.

Similarly to the binary mixture, TEM analysis reveals overall growth of the particles size after laser treatment of Gd–Si–Ge mixture with the formation of 3 major types of NPs: large nearly uniform spherical particles with a diameter over 50 nm (type A), hollow NPs (type B) and small NPs that mainly form aggregates surrounding larger NPs (type C in Figure 5). The increase in the NPs size can be the evidence of co-melting of small NPs as the result of laser irradiation that was further proved by the SAED analysis of the particles group presented in Figure 5a. The formation of the $Gd_5Si_2Ge_2$ monoclinic phase was found by the pattern analysis as the reflections from the (2–31), (042), (1–53), (420), (431), (343) crystallographic planes were observed. According to the phase diagram, several structures can be formed in the $Gd_5Si_{1-x}Ge_x$ system having the orthorhombic or monoclinic structure depending on the Si:Ge ratio: for x in the range $0 < x < 0.5$, the preferable structure is orthorhombic, while the crystal structure changes to monoclinic for $x \geq 0.5$. It should be noted that the admixture of gadolinium carbide with the Gd_4C_5 orthorhombic structure was also found in the SAED pattern. The target $Gd_5Si_2Ge_2$ phase and admixture phases mainly constituted different morphological types of NPs, as that was further proved by the HRTEM analysis of the separate particles. The large particles (type A) were composed mainly of the target monoclinic $Gd_5Si_2Ge_2$ phase confirmed by the observation of interplanar spacing of 2.86 Å, corresponding well to the reflection from the (2–31) plane. The hollow NPs (type B) were formed mainly of hexagonal Gd and its oxide. The small NPs (type C) are formed of the initial Gd, Si and Ge along

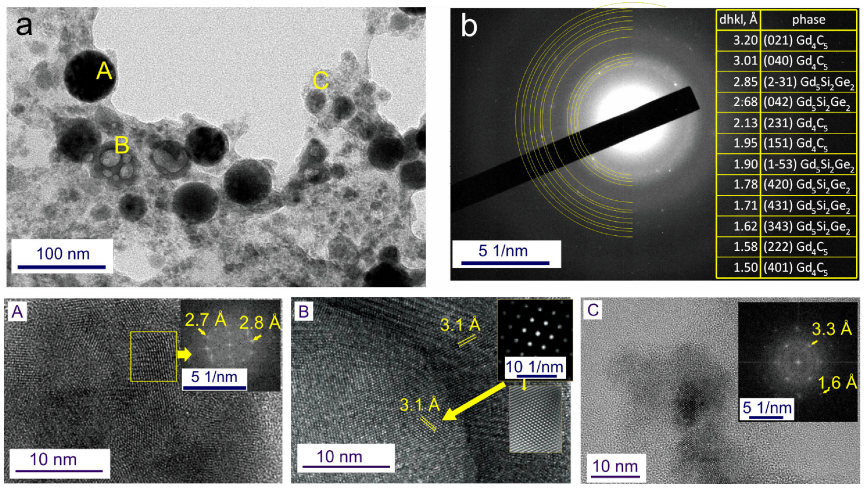

Figure 5. The results of TEM characterization of the NPs in Gd–Si–Ge mixture after 532 nm laser irradiation: (a) TEM image with A,B,C indicating different NPs types further analyzed by HRTEM; (b) SAED pattern of the group of the NPs presented in Figure 5a with the results of its indexing summarized in the inset table, A – HRTEM photograph of the selected area in the separate large nanoparticle with the result of the FFT processing, the dots on the FFT image correspond well to the (2–31) and (042) planes of the monoclinic $Gd_5Si_2Ge_2$ phase; B, C – HRTEM images of the separate hollow NP and small agregated NPs, respectively.

with hexagonal C phase as a product of ethanol decomposition.

Magnetic and magneto-thermal properties of the formed colloids were studied for the identification of their application possibility in self-controlled hyperthermia treatment of the tumors.

The magnetic properties are shown in Figure 6. As can be concluded from the analysis of the magnetization behavior in the external magnetic field (Figure 6a), the formed particles were soft ferromagnetic with coercivities <100 Oe at 280, 290 and 300 K (below T_C) and exhibited paramagnetic behavior at 310 K, above T_C as the magnetization curve at this temperature showed the sigmoidal shape without the hysteresis loop. The thermomagnetic curves (Figure 6b) allowed to estimate the Curie temperature of the formed NPs as the spontaneous magnetization exhibited the maximum change at T_C, so the derivative of magnetization with respect to temperature (dM/dT) showed a minimum at the Curie temperature (Figure 6c). The estimated value of the Curie temperature was found to be in the temperature range required for the application in the self-regulated magnetic hyperthermia. However, the magnetic transition is broadened, so the magnetization decreases significantly in the temperature range between 310 and 320 K. As the magnetization decreases, the heating should decrease

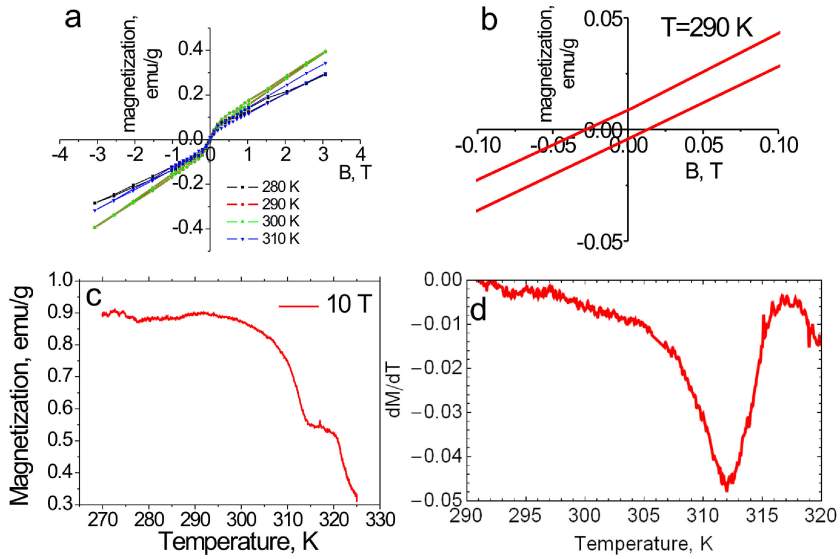

Figure 6. The magnetic measurements of the Gd–Si–Ge NPs after laser modification: (a) magnetic field dependencies of magnetization at temperatures of 280, 290, 300 and 310 K; (b) magnetization at low fields showing the hysteresis behavior of the magnetization at 290 K; (c) magnetization as a function of temperature at a magnetic field of 10 T; (d) $dM/dT = f(T)$ as a function of temperature used for estimation of the Curie temperature of the formed NPs (312 K).

not allowing the temperature to exceed T_C, so self-regulated regime can be achieved.

Thus, magnetization measurements showed that the developed technique based on the laser treatment of the mixture of the Gd, Si and Ge colloidal solutions provides the formation possibility of ternary Gd compounds with magnetic properties in the desired for hyperthermia temperature range and tuning the magnetic ordering temperature between 315 and 320 K by adjusting the composition of the prepared samples.

3. Conclusions

The paper provides the experimental findings of compound gadolinium silicides and gadolinium germano-silicides NPs formation by laser irradiation of the colloidal solutions mixture containing NPs of relevant elements. It is supposed that the compound NPs are formed in result of NPs heating, co-melting and chemical reactions in the liquid droplets. In order to estimate the role of the pulse duration on the processes initiated under laser irradiation, nanosecond and picosecond laser-induced modification at 532 nm was applied to the colloid mixtures. The transformation of separate NPs in the mixture into the compound ones under laser irradiation was confirmed by TEM, SAED and HRTEM analysis. In the case of the 10 ps laser irradiation, the alloying and compound formation was found to occur at lower laser pulse energies (10–50 μJ/pulse compared to 50–60 mJ/pulse, in the case of 10 ns excitation). Most probably, the higher energy threshold for nanosecond excitation compared to the picosecond case is due to the dissipation of the absorbed energy to the solvent during laser excitation.

Based on the hot NPs thermal radiation, the temperature of the laser heated particles was determined. The resulting temperature was shown to be described on the basis of a balance between the absorbed laser energy and heat losses during the laser pulse using the physical constants of the bulk materials.

Although the silicide phases are partially formed after simple mixing of Gd and Si colloids, laser processing of the mixture of solutions was shown to provide the better control over the silicide synthesis process. By varying the laser parameters such as laser pulse duration, fluence and chemical composition of the liquid, it is possible to achieve the optimal conditions for the synthesis of NPs with required composition and size well fitted to the selected purposes. For example, the synthesized binary (Gd–Si) and ternary (Gd–Si–Ge) compound particles exhibited the magnetic behavior promising for their potential biomedical applications, in particular, in the method of magnetic hyperthermia treatment.

Experimental Section

The initial Gd, Si and Ge colloids were prepared by laser ablation technique. Nd:YAG laser (LOTIS TII, LS2134D), operating in a double-pulse mode at 1064 nm (energy 80 mJ/pulse, repetition rate 10 Hz, pulse duration 8 ns) was used for ablation of the relevant target placed in the cell filled with ethanol. The experimental system used for NPs preparation was described in details in.[26,28] Briefly, the scheme of the experiment is explained in Figure 1.

The colloids of prepared single element NPs were mixed in the proportion corresponding to the atomic ratio Gd:Si = 5:4 or Gd:Si:Ge = 5:2:2. These colloid mixtures were subjected to laser irradiation by the second harmonic of the nanosecond Nd:YAG laser (wavelength 532 nm, pulse duration 10 ns, beam diameter 5.0 mm) with the power densities of 2.3×10^7 and 4×10^7 W/cm^2 (laser fluences 0.23 and 0.4 J/cm^2). The second set of experiments was done using the second harmonic of the picosecond Nd:YVO_4 laser (wavelength 532 nm, pulse duration 10 ps, beam diameter 4.0 mm) with the power ranging from 1 to 5.3 W (pulse power densities 0.8×10^7 and 4.2×10^7 W/cm^2, or laser fluences 0.08 and 0.42 mJ/cm^2, respectively). A mode-locked EKSPLA PL10100 laser was used in these experiments. For the laser-induced irradiation experiments, 3.0 mL of the NPs solution was placed in a 1 cm optical path quartz cuvette. As the order of mixing was previously found having an influence on the composition and morphology of the NPs formed,[26] the mixtures were prepared by the addition of Si colloid to Gd. The solutions were irradiated for 10 min, after that the absorption spectra were measured, and TEM samples were prepared. It should be noted that nanosecond and picosecond pulses with equal energies do not necessarily result in the same level of excitation because of the complicated time-dependent response of NPs to laser irradiation. Nevertheless, it was important to elucidate a possibility of using different commercially available laser sources for NPs modification.

The morphology and structure of the resulting NPs were analyzed by SAED, XRD, TEM and SEM techniques. To determine the temperature of NPs, their thermal radiation spectra were detected. For this purpose, the emission of the laser irradiated particles in the solution was collected with a lens (F = 61 mm) on the entrance slit of the spectrometer (S3801 SOLAR TII, Belarus focal length of 380 nm, grating 600 lines/mm, relative aperture of 1:4.9) with a CCD detector (Toshiba 1304AP, 3648 photosensitive elements with dimensions of 8×200 microns). The linearity of the system was verified using neutral filters. In order to reduce the noise introduced by fluctuations of radiation signal, averaging over 10 pulses was carried out. A tungsten strip calibration lamp was used for the optical detection system calibration. To determine the temperature of NPs based on their thermal radiation, the calibrated spectra were fitted by a Planck curve, taking into account the emissivity function of NPs and that the CCD detector counts the photon numbers.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: colloids · gadolinium · laser-induced chemical interactions · magnetic properties · nanoparticles

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