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Chemical Interactions in a Mixture of Gadolinium and Silicon Colloidal Solutions

Natalie Tarasenka [a,b], Vladimir Pankov [b], Nikolai Tarasenko [a,*]

[a] B.I. Stepanov Institute of Physics of National Academy of Sciences of Belarus, Nezaleznasti Ave., 220072 Minsk, Belarus
[b] Belarusian State University, 14 Leningradskaya Str, 220004 Minsk, Belarus

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ABSTRACT

We report about the chemical activity of Gd and Si nanoparticles in the mixture of their colloidal solutions. It was found that mixing of two colloids prepared by laser ablation technique results in the chemical interaction between nanoparticles and formation of silicide phases at room temperature. The phase composition of the resulting products was found to be dependent on the mixing order.

It is known that due to the high surface-to-volume ratio and surface free energy, particles with dimensions at the nanoscale have a strong tendency to coalescence even at much lower temperatures than their melting temperatures as they are put together [1,2]. This feature has been applied for the synthesis of the alloy nanoparticles (NPs) from metals which are immiscible in the solid or molten state [1–4].

The mechanism of the spontaneous alloying is generally interpreted in the framework of defect enhanced diffusion of the elements [5]. Indeed, the lattice of the NPs produced by different synthetic techniques is usually distorted that should favor interdiffusion of the components. The presence of a large number of surface atoms in NPs, defects at the interface or crystal facet changes can enhance the diffusion coefficient. Besides, spontaneous alloying of NPs can be attributed to the melting temperature decrease with the decrease in the particle size [6]. Nevertheless, the detailed kinetics of spontaneous alloying has not been fully elucidated and the interactions in the mixed dispersion of NPs depend on a number of factors, such as the size, surface state of the NPs, the nature of the bimetallic system and solution [4,7].

It should be noted that in the studies on the behavior of NPs in mixtures of colloidal solutions the main attention has been paid to the evolution of their microstructure and alloyed NPs formation, but to the best of our knowledge, there is no published reports on the chemical interaction between NPs and the formation of the compound particles.

In this paper we report about the chemical activity of Gd and Si NPs in the mixture of their colloidal solutions. It was found that a simple mixing of two colloids prepared by laser ablation technique leads to the chemical interaction between NPs and formation of silicide phases at room temperature. The phase composition of the resulting products was found to depend on the mixing order.

Gd based NPs are of current interest due to their magnetic properties and the potential peculiarities that the nanoscale or nanocomposite materials may exhibit due to their finite size and surface-interface effects. For example, nanoscale Gd, its compounds and alloys can be used as promising materials for applications as therapeutic agents in drug delivery [8,9] and hyperthermia treatment [10,11]. Compared to the materials traditionally used in hyperthermia treatment of tumors, like iron oxide, Gd silicide provides advantage of the heating in the self-controlled regime that makes them the most promising candidates for the hyperthermia application. Knowing the peculiarities of the chemical interactions between Gd and Si nanoparticles in colloidal solutions is important for optimization of the procedure of Gd silicide preparation.

The initial Gd and Si colloids were prepared by laser ablation technique in liquid. Nd:YAG laser (LOTIS TII, LS2134D), operating 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. After the preparation Gd and Si colloids were mixed in the proportion corresponding to the atomic ratio Gd:Si = 5:4. In order to determine the influence of the mixing order on the process of compound NPs formation, the morphology, composition and structure of the particles prepared by adding Si to Gd and Gd to Si colloids were analyzed by SAED, TEM, HRTEM and FTIR techniques.

The results of the as-prepared NPs morphology studies are shown in Fig. 1. As can be concluded from the TEM images, the prepared Gd and Si NPs are of an overall quasi-spherical morphology and are rather small in size (the average diameter is 5 nm for Si and 10 nm for Gd). However, Gd NPs form aggregates with irregular shape and size more than 100 nm while Si NPs are well-separated and had a narrow size distribution.

* Corresponding author.
E-mail address: n.tarasenko@ifanbel.bas-net.by (N. Tarasenko).

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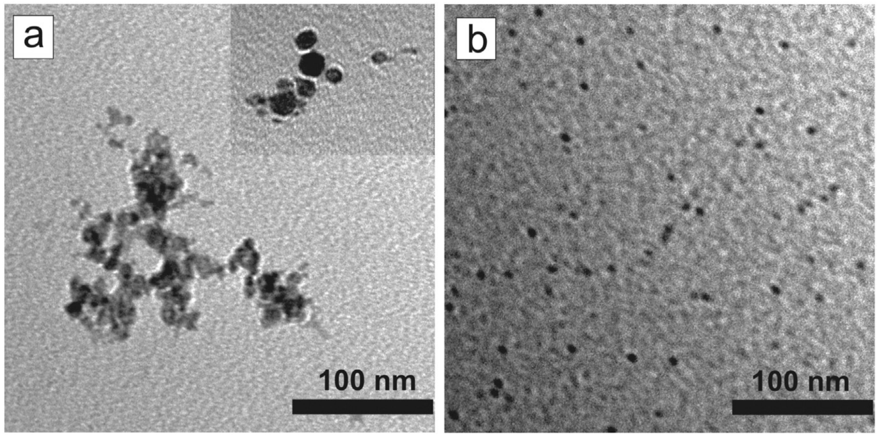


Fig. 1. TEM images of Gd (a) and Si (b) NPs prepared by laser ablation in ethanol.

Addition of silicon colloidal solution to the Gd colloid results in the drastic change in the morphology and structure of the NPs. As can be seen in Fig. 2, several types of NPs appeared: in addition to the small spherical particles, that mostly form aggregates, large near-spherical particles with the diameter more than 70 nm and hollow NPs are formed. The change in morphology (the growth in size) of the particles after mixing can be indicative of their aggregation and coalescence with possible chemical processes between the particles.

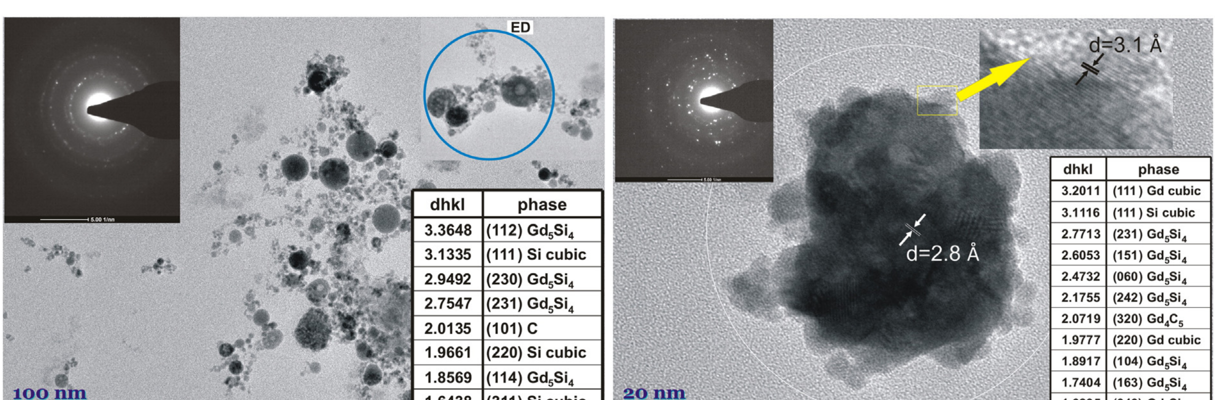
The analysis of the SAED patterns of the mixed samples proves that NPs are mostly polycrystalline as well-defined rings are seen in the patterns. However, different types of NPs that are formed after mixing of the colloidal solutions have different composition and crystal structure. Hollow nanoparticles that are shown in Fig. 2 have no Gd phases in their composition while (111), (220) and (311) reflections of cubic silicon are present in the pattern. The formation of the binary Gd_5Si_4 compound is proved by the presence of the reflections from (112), (230), (231) and (114) planes of the orthorhombic Gd_5Si_4 phase (space group *Pnma*, No. 62) [12].

The HRTEM studies of the single particle with diameter more than 100 nm (Fig. 2b) shows that its composition is not uniform throughout the entire volume and the particle can be considered as an aggregate of smaller particles. The analysis of the HRTEM image using the Fourier transformations revealed that the shell of cubic silicon NPs is formed on the periphery of the aggregate. The interplanar distances are measured to be about 0.31 nm, corresponding to the (111) crystal planes of the cubic Si, while the interplanar distances in another direction are measured to be about 0.19 nm, corresponding to the (220) crystal planes of the cubic Si [13].

In the central part of the particle the area with interplanar distance of 2.8 Å corresponding to the (231) plane of orthorhombic Gd_5Si_4 was found. Observation of several rings in the diffraction patterns allowed determining the lattice parameters of the prepared NPs. The calculated values were found to be $a = 7.42$ Å, $b = 14.84$ Å, $c = 7.82$ Å that is in a good agreement with the reported ones ($a = 7.4857$ Å, $b = 14.750$ Å, $c = 7.7514$ Å) for orthorhombic Gd_5Si_4 [14].

It should be noted that trace amount of carbon (Fig. 2a) or gadolinium carbide (Fig. 2b) phases can also be formed in result of the partial decomposition of ethanol during laser ablation and its reaction with gadolinium.

The order of mixing of the colloidal solutions was found to be the factor that influences the phase composition of NPs in the mixture. As can be concluded from Fig. 3 the morphology of the NPs in mixture does not significantly change with varying of the mixing order. As in the previous case aggregates of small spherical nanoparticles, hollow nanoparticles as well as large near-spherical nanoparticles with non-uniform composition are formed. The analysis of SAED pattern of NPs formed in the mixture of Gd and Si colloids when Gd colloid was added to Si one (Fig. 3a) revealed the formation of the mixture of silicides of Gd_5Si_4 and $GdSi_2$ composition. Besides, some diffraction spots could be assigned to the (111), (220) and (311) planes of cubic Si [13]. It should be noted the orthorhombic GdSi phase has only been found in the large separate spherical NPs formed after mixing of Gd



dhkl	phase
3.3648	(112) Gd_5Si_4
3.1335	(111) Si cubic
2.9492	(230) Gd_5Si_4
2.7547	(231) Gd_5Si_4
2.0135	(101) C
1.9661	(220) Si cubic
1.8569	(114) Gd_5Si_4
1.6438	(311) Si cubic

dhkl	phase
3.2011	(111) Gd cubic
3.1116	(111) Si cubic
2.7713	(231) Gd_5Si_4
2.6053	(151) Gd_5Si_4
2.4732	(060) Gd_5Si_4
2.1755	(242) Gd_5Si_4
2.0719	(320) Gd_4C_5
1.9777	(220) Gd cubic
1.8917	(104) Gd_5Si_4
1.7404	(163) Gd_5Si_4
1.6235	(343) Gd_5Si_4

Fig. 2. (a) TEM image of NPs in the mixture of Si and Gd colloidal solutions when Si colloid was added to Gd one. The inset shows the SAED pattern of the selected group of NPs, (b) TEM image and the SAED pattern of the relatively large aggregate formed in the mixture of Si and Gd colloids after adding of Si colloid into Gd colloidal solution.