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Annealing of PrF_3 Nanoparticles by Microwave Irradiation

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Abstract—The influence of microwave irradiation on the recovery of nanocrystalline PrF_3 powders has been experimentally analyzed by nuclear magnetic resonance (NMR) at $T = 1.5$ K. It is established that the relaxation times of ^{141}Pr and ^{19}F nuclei rise significantly with an increase in the hydrothermal-treatment time, whereas the ^{141}Pr NMR spectra narrow, which indicates a decrease in the number of defects in the lattices of nanosamples.

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It is known that, when passing from a bulk material to nanoparticles, the parameters of the former change significantly and new unique properties may arise [1–3]. The synthesis and investigation of nanocrystals of rare-earth trifluorides are of great interest due to the unique magnetic, electric, and optical properties of these objects. Many techniques for synthesizing nanoparticles (mechanosynthesis, detonation synthesis, electric explosion, plasma-chemical synthesis, self-propagating high-temperature synthesis, vapor-phase synthesis, thermal decomposition and recovery, deposition from colloidal solutions, etc.) and changing their structure have been approved [4].

Deposition from colloidal solutions was the first method to prepare nanoparticles. It implies a rapid chemical reaction between the solution components with its interruption at a certain instant, after which the dispersed system is transferred from liquid colloidal state into dispersed solid one. One of the simplest, fastest, and most efficient ways of changing the nanoparticle structure is the hydrothermal treatment of colloidal solutions. Various nanostructures (nanotubes, fullerene-like nanoparticles, etc.) can be formed by varying the synthesis parameters, such as temperature, treatment time, and pressure. Using this technique, lanthanide fluorides LnF_3 (Ln = La–Lu) were synthesized and characterized in [5]. The basic concept of this work was to place a colloidal solution with nanoparticles in an autoclave (temperature ~180°C) for ~24 h. This technique was modified by replacing the autoclave with a microwave oven (power ~650 W, exposure time ~20 min) [6]. It was shown that nanoparticles subjected to hydrothermal synthesis acquire a fullerene-like shape; however, the mechanism of the influence of microwave radiation on nanoparticles has not been studied.

We tested a method for varying the size of PrF_3 nanoparticles by changing the time of hydrothermal treatment in a microwave oven. The method for synthesizing samples was described in detail in [7, 8], where the size distributions of particles and the X-ray diffraction spectra were also reported. Water clusters were found in PrF_3 nanosamples, and their size was determined by nuclear magnetic resonance (NMR) cryoporometry and high-resolution transmission microscopy [9]. A nuclear pseudoquadrupole resonance of ^{141}Pr was observed for the first time, the parameters of the nuclear-spin Hamiltonian were determined, and the parameters of the crystal electric field in nanocrystals and microcrystals were found to differ significantly [10]. The spin kinetics of adsorbed and liquid ^3He in contact with crystalline nanopowders of Van Vleck paramagnet PrF_3 was studied by NMR methods at 1.5 K. The parameters of nuclear magnetic relaxation of ^3He were found to correlate with the particle sizes. A qualitative model of magnetic relaxation of ^3He was proposed in [8, 11] to describe the experimental data.

According to the aforementioned technique, we synthesized five samples of PrF_3 nanopowders with different times of hydrothermal treatment of colloidal solution in a microwave oven. Using the data of high-resolution transmission electron microscopy, we

Average size of nanoparticles of a series of PrF_3 samples in dependence of the time of hydrothermal treatment of colloidal solution by microwave irradiation

PrF_3 sample number	1	2	3	4	5
Microwave irradiation time, min	0	20	40	60	420
Diameter, nm	21 ± 9	31 ± 10	27 ± 10	37 ± 10	34 ± 13

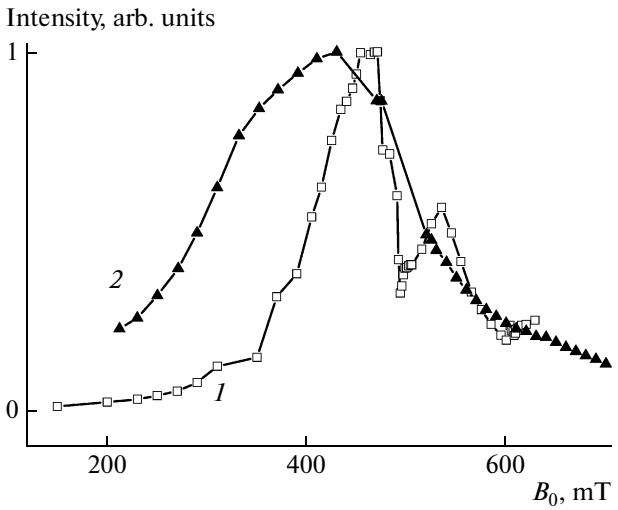

Fig. 1. ^{141}Pr NMR spectra of PrF_3 powders: (*1*) microsample (45 μm) and (*2*) nanosample no. 2 (frequency 19.5 MHz, temperature 1.5 K).

determined the size distribution of nanoparticles (see table).

All our experimental results were obtained on a home-build NMR spectrometer described in [12]. The temperature of the samples in all experiments was 1.5 K. The ^{141}Pr NMR spectra were recorded by measuring the spin-echo amplitude as a function of applied external magnetic field. To obtain the spin echo of nuclei, we used the following sequence of RF pulses: $\tau_{\pi/2} - \tau - \tau_\pi$ ($\tau = 25$ μs, $\tau_{\pi/2} = 1$ μs). The spin–lattice relaxation times were measured using the "saturation–recovery" technique.

Figure 1 shows the ^{141}Pr NMR spectra of microsized (45 μm) and nanosized (sample no. 2, average particle size 31 nm, hydrothermal-treatment time 20 min) PrF_3 powders. It can be seen that the spectrum of nanosample no. 2 is much wider than that of the microsample, which indicates a much larger number of defects in the crystal structure of the former. Since defects may influence the longitudinal-magne-

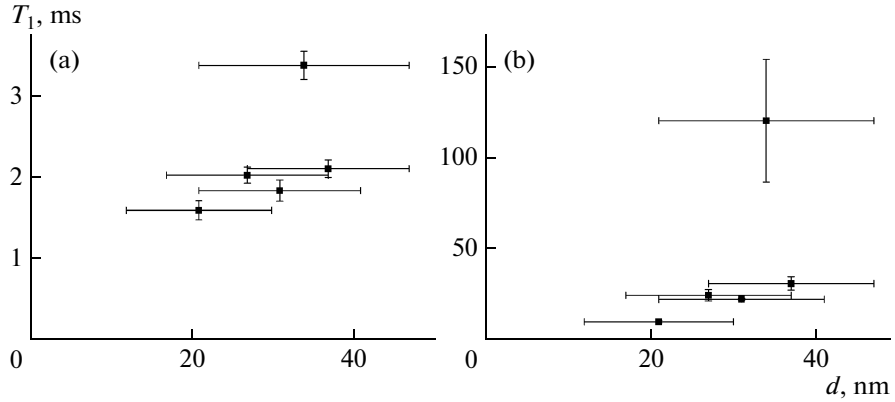

Fig. 2. Measured dependences of relaxation times T_1 of longitudinal magnetization of (a) ^{141}Pr nuclei in a magnetic field of 120 mT and (b) ^{19}F nuclei in a magnetic field of 170 mT in PrF_3 on the particle size (frequency 6.63 MHz, 1.5 K).

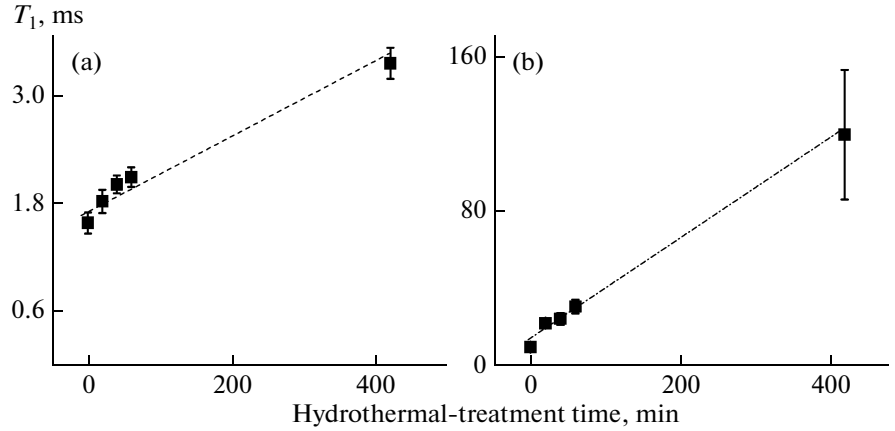

Fig. 3. Dependences of relaxation time T_1 of the longitudinal magnetization of (a) ^{141}Pr nuclei in a magnetic field of 120 mT and (b) ^{19}F nuclei in a magnetic field of 170 mT in PrF_3 nanopowders on the hydrothermal-treatment time (frequency 6.63 MHz, 1.5 K). The dashed line shows the eye-guide.

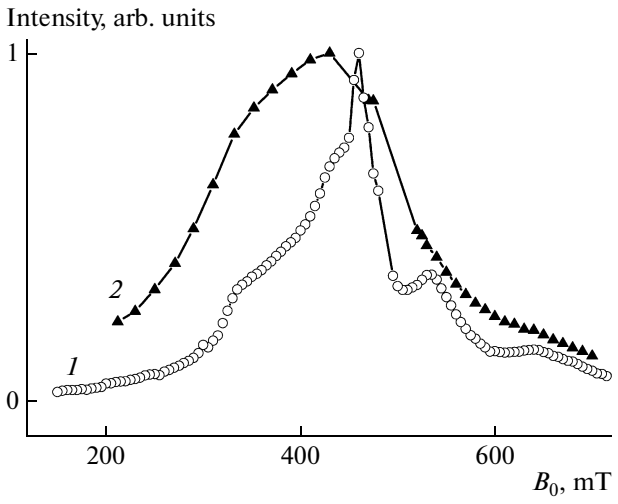

Fig. 4. ^{141}Pr NMR spectra of PrF_3 nanopowders: (*1*) nanosample no. 5 (average particle size 34 nm, hydrothermal-treatment time 420 min) and (*2*) nanosample no. 2 (average particle size 31 nm, hydrothermal-treatment time 20 min); the frequency is 19.5 MHz, and the temperature is 1.5 K.

tization relaxation, we performed relaxometry experiments on ^{141}Pr and ^{19}F nuclei.

Figure 2 shows dependences of experimental times of longitudinal-magnetization relaxation of ^{141}Pr and ^{19}F nuclei in PrF_3 on the particle size. It can be seen that the nuclear spin–lattice relaxation times of ^{141}Pr and ^{19}F do not correlate with the particle size, which indicates primarily uniform distribution of defects over the particle structure.

A model implying capture of water molecules in the lattice during fast growth of nanoparticles in chemical reaction in an aqueous solution was proposed in [9]. Further treatment by microwave radiation is likely to make the water molecules propagating through the lattice form clusters. At the same time, the nanoparticle structure is transformed and particles become more homogeneous. This restructuring should improve the quality of the crystal structure and, accordingly, increase the nuclear spin–lattice relaxation times of ^{141}Pr and ^{19}F, depending on the hydrothermal-treatment time.

Figure 3 shows the same experimental values of relaxation times of longitudinal magnetization of ^{141}Pr and ^{19}F nuclei in PrF_3 as in Fig. 2, but in dependence on the time of hydrothermal treatment by microwave radiation. It can be seen that the relaxation time of longitudinal magnetization of ^{141}Pr and ^{19}F nuclei in PrF_3 nanosamples correlates with the hydrothermal-treatment time. Restructuring the samples and the decrease in the number of defects in the crystal structure under microwave irradiation should affect the ^{141}Pr NMR spectra.

Figure 4 shows the ^{141}Pr NMR spectra of nanosamples nos. 2 (31 nm, hydrothermal-treatment time 20 min) and 5 (34 nm, hydrothermal-treatment time 420 min). It can be seen that the spectrum narrows significantly with an increase in the hydrothermal-treatment time.

NMR spectroscopy and relaxometry experiments on five synthesized PrF_3 nanosamples demonstrate that microwave irradiation of a colloidal solution affects the particle restructuring. It was shown that relaxation times T_1 of ^{141}Pr and ^{19}F nuclei increase significantly with an increase in the hydrothermal-treatment time, whereas the ^{141}Pr NMR line narrows, which indicates a decrease in the number of defects in the nanosample lattice. Thus, the treatment of PrF_3 colloidal solutions by microwave irradiation during synthesis is in fact annealing of crystal-structure defects in nanosamples.

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