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Research Article

Microwave-Assisted Hydrothermal Synthesis and Annealing of DyF_3 Nanoparticles

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The series of DyF_3 nanosized samples was synthesized by the colloidal chemistry method. The microwave-assisted hydrothermal treatment was used for the first time for the modification of DyF_3 nanoparticles. Transmission electron microscopy images show that the DyF_3 nanoparticles have average particle size of about 16–18 nm and the size distribution becomes narrower during the microwave irradiation. The X-ray diffraction analysis shows the narrowing of the diffraction peaks versus microwave treatment time. The experimental data demonstrates restructuring of the nanoparticles and their crystal structure becomes closer to the ideal DyF_3 regular structure during the microwave irradiation of colloidal solution. The defect-annealing model of the microwave-assisted hydrothermal modification process is suggested.

1. Introduction

Several dozen research papers dedicated to LnF_3 nanosized samples synthesis have been published in recent years. Nowadays the lanthanide fluoride nanoparticles attract scientific interest because of their possible applications in many areas such as lasers, biolabels, and optical amplifiers [1–12]. The autoclave hydrothermal treatment is often used for structure and size modification of the lanthanide nanoparticles. The microwave-assisted synthesis of PrF_3 nanoparticles was suggested by Ma et al. [13] and modified at Kazan Federal University (Kazan, Russia). The PrF_3 nanoparticles size and structure dependence on the microwave-assisted hydrothermal treatment time were obtained by the high-resolution transmission electron microscopy (TEM), nuclear magnetic resonance (NMR), and electron paramagnetic resonance [14–21].

The other trifluoride compound of great interest is DyF_3. Recent research showed that DyF_3 powders could significantly improve the properties of Nd-Fe-B magnets [22–25]. In addition, DyF_3 is an important component of oxyfluoride glasses [26]. On the other hand, there is a ferromagnetic phase transition in a single crystal at $T_c = 2.55$ K [27]. Investigation of Curie temperature dependence versus the size of DyF_3 nanoparticles is a fundamental problem. There are only few reports about DyF_3 nanoparticles synthesis [28–30] and the size modification was achieved by the autoclave technique.

The aim of the present work is a synthesis and modification of DyF_3 nanoparticles using the microwave-assisted hydrothermal treatment method.

2. Materials and Methods

Sodium fluoride NaF (99.9%) and dysprosium oxide Dy_2O_3 (99.99%) were obtained from Sigma-Aldrich. The nanosized DyF_3 samples #1–3 were synthesized by similar method as for PrF_3 nanoparticles synthesis [14, 15]. In a typical synthesis, 6.2 g of powdered dysprosium oxide Dy_2O_3 was dissolved in 400 mL of 10% nitric acid HNO_3 aqueous solution to form a transparent solution

$$\begin{aligned} &Dy_2O_3\,(s) + 6HNO_3\,(aq) \\ &\quad \longrightarrow 2Dy\,(NO_3)_3\,(aq) + 3H_2O\,(l) \end{aligned} \tag{1}$$

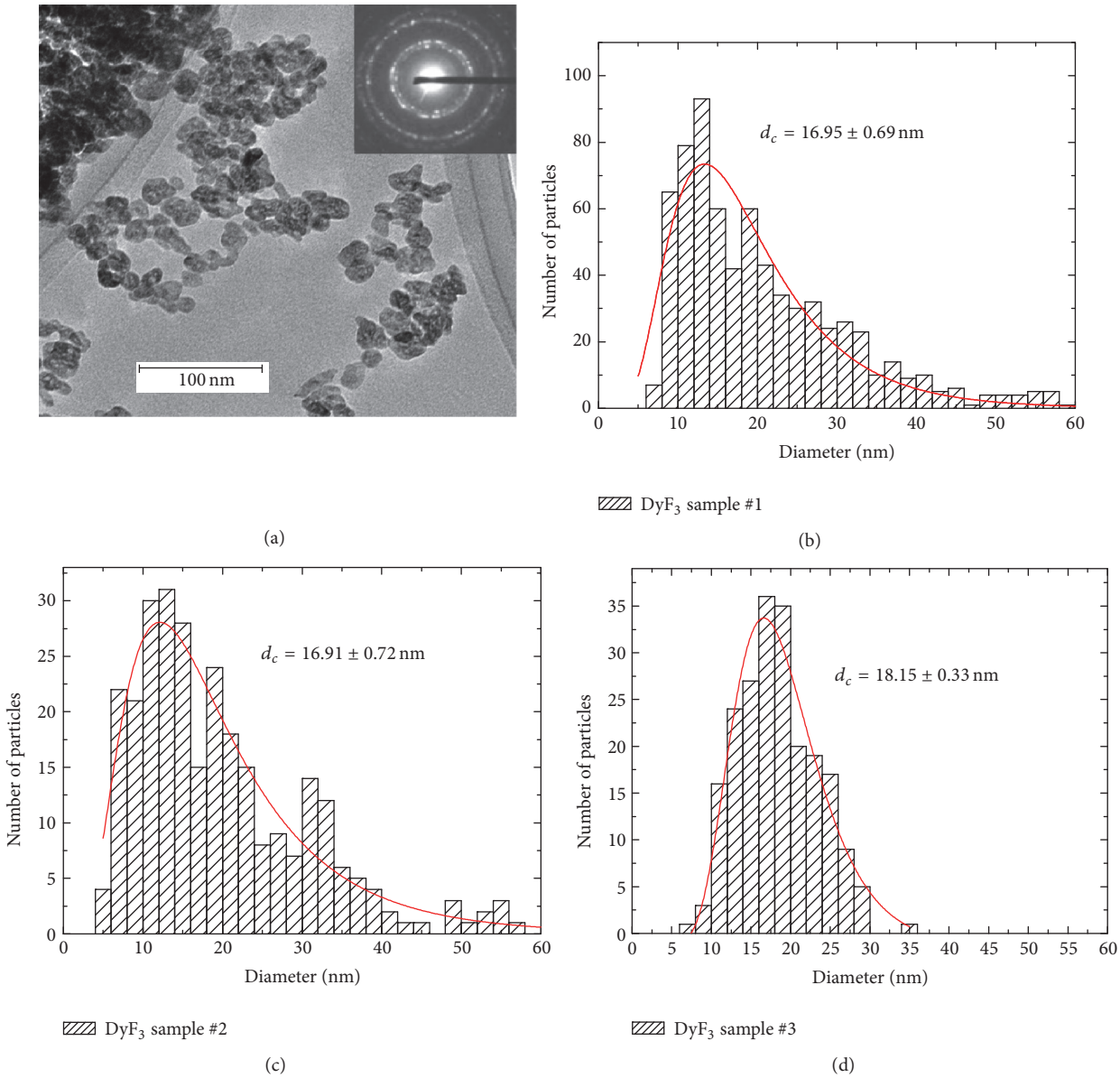

Figure 1: (a) TEM image of DyF_3 nanoparticles with corresponding electron diffraction pattern in the insert (sample #3). (b)–(d) The size distribution diagrams for all samples. Solid line is the log-normal distribution fitting, and d_c is the center.

Then, after filtering, 4.75 g of sodium fluoride NaF (F : Dy = 3 : 1) was added into the abovementioned solution under violent stirring. A white colloidal precipitate of DyF_3 appeared immediately.

$$\begin{aligned} &Dy(NO_3)_3\,(aq) + 3NaF\,(s) \\ &\longrightarrow DyF_3\,(s) + 3NaNO_3\,(aq) \end{aligned} \tag{2}$$

The pH of the suspension was adjusted by 25% ammonia aqueous solution (about 4.0–5.0). Deionized water was filled into the suspension to make the volume up to 750 mL. After stirring for about 20 min, the suspension was finally transferred into a 1 L round flask (synthesis of sample #1 has been stopped at this stage). Part of the solution was placed into the microwave oven (650 W, 2.45 GHz) for further hydrothermal treatment (sample #2). The suspension was put into the microwave oven at 70% of the maximum power for 30 minutes. The resulting product was collected by centrifugation (Janetski K24; 12000 RPM) and washed using the deionized water for several times.

Finally, the solution was dried out on the flat surface in air at room temperature. Sample #3 was prepared by the same method and treated by the microwave irradiation for 420 minutes.

TEM images of nanosized samples were obtained by using Philips CM300 operated at 300 kV (Neel Institute, Grenoble, France). Powder X-ray diffraction was done by Bruker D8 Advance X-ray diffractometer with use of copper Ka (α = 1.5418 Å) radiation and continuous scan (scan speed 0.005 degrees per second in the range of diffraction angles 20–60 degrees).

3. Results and Discussion

Figure 1 shows the TEM image with the corresponding electron diffraction pattern in the insert (sample #3) and size

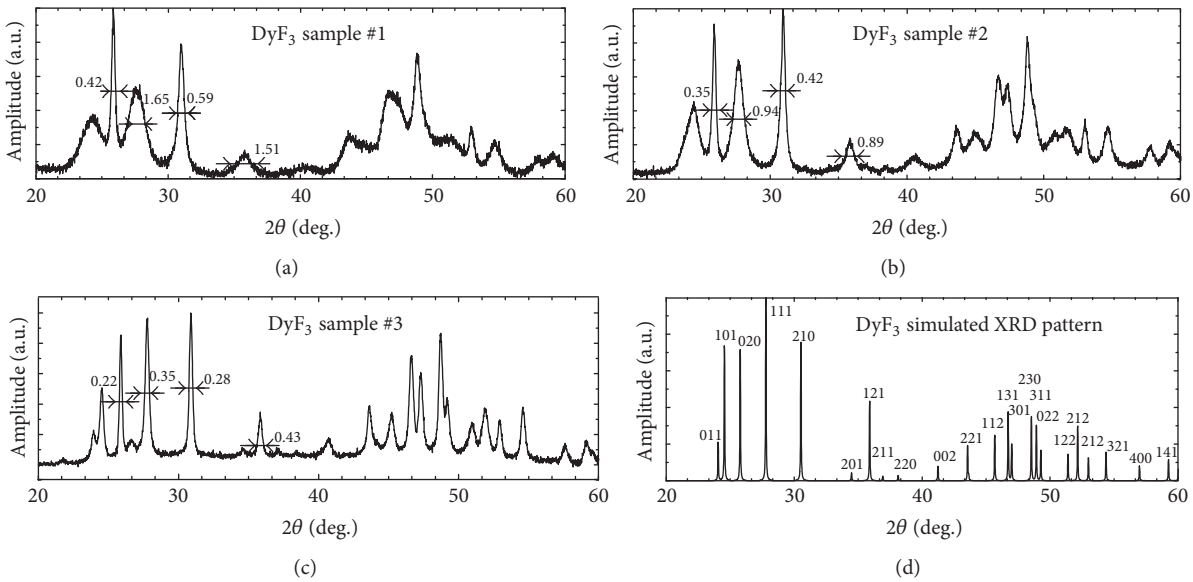

Figure 2: (a)–(c) Experimental XRD patterns of synthesized DyF_3 nanosized samples #1–3. (d) simulated XRD patterns in PowderCell software.

distribution diagrams for all samples. The sharp diffraction rings show the crystal particles presence (rings radii: 0.36 nm, 0.32 nm, and 0.20 nm). All diagrams were fitted by the log-normal distribution. The synthesized nanoparticles have average size of about 16–18 nm (sample #1, 16.9 nm; sample #2, 16.9 nm; sample #3, 18.2 nm). There is no significant DyF_3 nanoparticles size dependence on the microwave-assisted hydrothermal treatment time unlike the case of PrF_3 sample [20]. Clearly, the size distribution becomes narrower during the microwave irradiation. In the case of the microwave-assisted synthesis of PrF_3 nanoparticles, the restructuring of particles was observed earlier by NMR [20]. It was interesting to see the crystal structure changes in the process of DyF_3 nanosized samples treatment.

Crystal structure of DyF_3 nanoparticles was characterized by X-ray diffraction (XRD). Experimental XRD patterns of three DyF_3 nanosized samples are shown in Figure 2. Diffraction peaks could be indexed from the simulated pattern calculated by PowderCell [31] software (space group Pnma (No. 62), lattice constants $a = 0.6460$ nm, $b = 0.6906$ nm, and $c = 0.4376$ nm [32]). Obviously, sample #1 (Figure 2(a)) has wide peaks and after 30 minutes of the microwave-assisted hydrothermal treatment the peaks becomes narrower (Figure 2(b)). After 7 hours of treatment the XRD pattern became even narrower (Figure 2(c)). High and sharp peaks indicate high crystallinity of nanoparticles for sample #3.

The analysis of obtained experimental data suggests the following hypothetical picture of the microwave-assisted hydrothermal modification process. Sample #1 has many defects of crystal structure because of the explosive character of the colloidal reaction. Further microwave treatment of the colloidal solution leads to local heating of DyF_3 particles. Some bigger particles crack into smaller ones, making the size distribution narrower, but the local restructuring continues further. The restructuring leads to decrease in the number of crystal structure defects.

The obtained results of restructuring process are different from that of PrF_3 nanoparticles, where the weak size dependence [20] and absolutely no difference in XRD patterns were observed. One of the possible reasons for difference of the microwave-assisted hydrothermal treatment's results between DyF_3 and PrF_3 nanoparticles may be the different symmetry (DyF_3 – orthorhombic D_{2h}^{16}-Pnma; PrF_3 – hexagonal C_{6v}^{3}-$P6_3cm$). Another reason could be the difference of lattice energies for lanthanide ions Pr and Dy [33].

The type of crystal structure defects is also different. In the case of PrF_3 nanoparticles—point defects, for DyF_3 nanoparticles—the defects are more severe. Annealing of the defects of the crystal structure of DyF_3 nanoparticles leads to significant (2–5 times) narrowing of XRD peaks. Usually the width of XRD peaks is related to the nanoparticles size and microstrains. There are various methods of X-ray analysis such as Scherrer [34], Williamson-Hall [35], and Warren-Averbach [36] methods. The average nanoparticles size was calculated using Debye-Scherrer's formula:

$$D = \frac{K\lambda}{\beta_{hkl}\cos\theta}. \tag{3}$$

For synthesized DyF_3 nanoparticles, the estimation gives too high values (ex., for sample #3 55 nm), which supports the defect nature of XRD peaks linewidth.

The analysis of XRD pattern by Williamson-Hall method also gives too high values for the average size of nanoparticles and attempts to estimate lattice distortions do not give reliable results. Warren-Averbach analysis is suitable for resolved XRD peaks and in our case is not applicable.

4. Conclusions

In summary, the series of DyF_3 nanoparticles was successfully synthesized by the microwave-assisted colloidal hydrothermal method for the first time. The nanoparticles were characterized by TEM and XRD. The average size of particles is about 16–18 nm and the size distribution becomes narrower after the microwave treatment. It was observed that the microwave irradiation treatment strongly affects the width of XRD peaks. They become narrower with the microwave treatment. The defect-annealing model of the microwave-assisted hydrothermal modification process is suggested.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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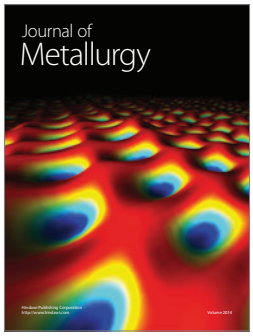

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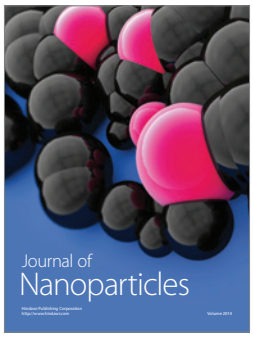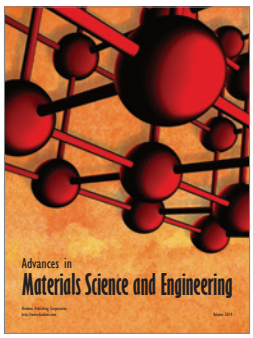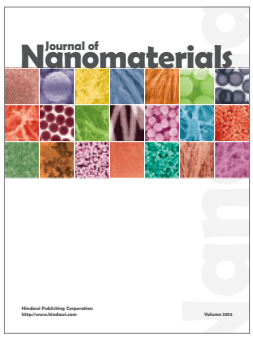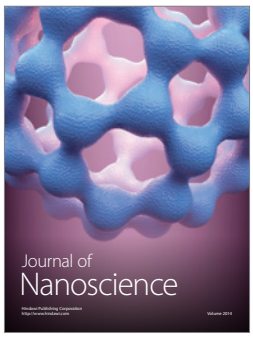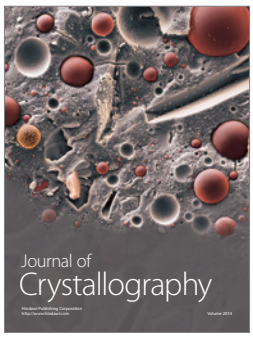
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