# Synthesis of Lanthanum Fluoride Nanocrystals and Modification of Their Surface

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**Abstract**—The LaF<sub>3</sub> nanoparticles were synthesized in the presence of citric acid and glycine. The products were characterized by X-ray phase analysis, transmission electron microscopy, dynamic light scattering, and infrared spectroscopy. In the presence of organic acids the synthesis was shown to result in a decrease in size of the formed particles. The IR spectroscopic studies revealed that citric acid and glycine acted as modifiers of the surface of LaF<sub>3</sub> particles forming a chemical bond with the surface ions La<sup>3+</sup>. A suggestion was advanced on the structure of the grafted surface layer. The features of the colloidal behavior of the systems were investigated.

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Nano-sized crystals of ionic inorganic compounds belong to the least studied class of inorganic nanomaterials. The only exceptions are semiconductors of A<sup>II</sup>B<sup>VI</sup> and A<sup>III</sup>B<sup>V</sup> structure, although in this respect also there are many unsolved problems.

The rare-earth element fluorides which are insoluble in water and biological fluids are of particular interest for the purposes of medical diagnostics. In particular, in [1] the synthesis was described of  $GdF_3$ nanoparticles for the application in magnetic imaging. On the basis of europium fluoride luminescent materials for diagnostics can be created. In extension of our studies on the europium fluoride [2], in this work we studied the methods of synthesis of the LaF<sub>3</sub> nanoparticles, the modification of their surface, and the colloid-chemical behavior of the objects obtained.

The most common method of synthesis of nanocrystals of water-insoluble salts is the exchange reactions in solution. The size and morphology of the resulting nanoparticles depend on several parameters, primarily on the concentration of reacting solutions, temperature, and order of the addition of the reagents. These particles, which can be conventionally termed as primary, are capable of association with each other to form larger aggregates up to precipitation.

In this study, we used two methods of synthesis: the slow addition of solution of  $La^{3+}$  salt to a solution of

NaF (method *I*, used, in particular in [1,2]) and the socalled double-drop method [3] that consists in the simultaneous slow addition of solutions of reagents to a large volume of water (method 2). In the second case one can expect to obtain smaller particles and their more narrow distribution due to the strong dilution of the initial reagents and maintaining unchanged reaction conditions in the course of time. In the synthesis of LaF<sub>3</sub> we varied the technique and the temperature of the reaction mixture. Comparative characteristics of the products are listed in Table 1.

The X-ray diffraction analysis confirmed the formation of LaF<sub>3</sub> phase with a hexagonal structure (JCPDS no. 32-0483, space group  $P\overline{3}c1$ ) in all syntheses. The most intense reflection corresponds to the interplanar distance d = 3.23 Å (face 111) [4]. No reflections of other phases or impurities were detected by the XRD. The relatively low intensity of reflections and their broadening indicate a polycrystalline nature of samples and a small size of the crystals. The data on the size of the primary particles obtained from the X-ray photographs with the Scherrer equation, the transmission electron microscopy (TEM), and the dynamic light scattering (DS) presented in Table 1 indicate that simultaneous adding of reagents to the aqueous solution results in the formation of the particles with a narrow size distribution. Increasing the reaction temperature from 20 to 75°C leads to a

Method of synthesis	Temperature, °C	Size of primary particles, nm		Average particle size nm
		X-ray phase analysis	Transmission electron microscopy	(dynamic light scattering)
Method 1	20	18	5-20	250
	75	20	5-30	150
Method 2	20	13	5-15	180
	75	16	10-30	100

Table 1. Comparative characteristics of the synthesized samples of LaF<sub>3</sub>

relatively small increase in the size of primary particles, reduces the extent of their aggregation, and results in the formation of more ordered crystals. Primary LaF<sub>3</sub> particles synthesized at 75°C have a regular hexagonal structure, in contrast to the particles obtained at 20°C (see the figure).

In all cases, the colloidal system formed was unstable: there was precipitation of lanthanum fluoride. The traditional method of stabilizing the nanopowder particles is a chemical modification of their surface. For the ionic crystals it is logical to use as modifiers complexing organic compounds capable to form coordination bonds with the metal ions on the surface.

In the present work we used citric acid and glycine as the modifiers. Proceeding from the above data, the synthesis of modified LaF<sub>3</sub> particles was carried out by method 2 at 75°C *in situ*, that is, by adding dropwise NaF and LaCl<sub>3</sub> solutions to the solution of a modifier.

The obtained colloidal systems of modified lanthanum fluoride are significantly more stabile than the unmodified samples. Their study by the DC method showed that in the presence of the modifier the size of aggregates was reduced to 60–80 nm, and the particle size distribution became narrower. For the precipitation of these particles we used ultracentrifugation or addition of alcohol or acid solution (in the case of modification with citric acid).

The isolated Citr@LaF<sub>3</sub> and Gly@LaF<sub>3</sub> powders were characterized by X-ray diffraction, transmission electron microscopy, and IR spectroscopy. Calculations of the Debye patterns showed the same phase composition in all cases that corresponded, as in the case of the synthesis in the absence of modifier, to the hexagonal LaF<sub>3</sub>. The distribution of point reflections along the circles indicates the polycrystalline nature of the modified samples and their lower ordering compared with the unmodified ones.

At the same time, the infrared spectroscopy showed the presence of molecules of the ligand in the products. Table 2 shows the values of the principal absorption bands in the infrared spectra of LaF<sub>3</sub>, citric acid CitrH<sub>3</sub>, and the modified sample Citr@LaF<sub>3</sub>, and their assignment. In the spectra of unmodified LaF<sub>3</sub> the bands of stretching and bending vibrations occur of water molecules forming a crystal hydrate with lanthanide fluoride and adsorbed on the particle surface, and the vibrations of the La–F bond. After modification, in the spectra appear the bands



The images of LaF<sub>3</sub> nanoparticles synthesized by (a) method 2 at 20°C and by method 1 at (b) 20°C and (c) 75°C obtained by transmission electron microscopy.

LaF <sub>3</sub>	CitrH <sub>3</sub>	Citr@LaF <sub>3</sub>	Assignment [5, 6]
3600-3200		3600-3200	$v_{OH}(H_2O)$
	3496		$v_{C-OH}(\alpha$ -hydroxy group)
	2665		v <sub>OH</sub> (COOH dimers)
	1755, 1728, 1703		v <sub>as</sub> (COOH),
1637			$\delta(H_2O)$
		1591, 1583, 1571	$v_{as}(COO^{-})$
	1429, 1390, 1360		v <sub>s</sub> (COOH)
		1458, 1438, 1420, 1411	v <sub>s</sub> (COO <sup>-</sup> )
	1292, 1173	1303, 1255, 1188	$\rho_r(CH_2), \rho_\tau(CH_2), \rho_\omega(CH_2)$
	1082	1078	$v_{C-OH}(\alpha$ -hydroxy group),
			$v_{C-O}$ (carbonyl), $v_{C-C}$
		561	$\delta(COO^{-}) + \delta(LaOC)$
	505		$\rho_r(COO^-)$
419, 411		408	δ(LaF)

Table 2. Assignment of vibration frequencies (cm<sup>-1</sup>) in the IR spectra of LaF<sub>3</sub>, citric acid CitrH<sub>3</sub>, and Citr@LaF<sub>3</sub>

characteristic of citric acid: vibrations of carboxy, hydroxy, and C-H groups. The decrease in the vibration frequencies of the carboxy groups in the spectra of Citr@LaF<sub>3</sub> compared with citric acid indicates that they are in the deprotonated, ionized state. The difference between the frequencies of asymmetric and symmetric stretching vibrations of the coordinated carboxy group,  $\Delta = v_{as}(COO^{-}) - v_{s}(COO^{-})$ , can be used as a criterion showing how the carboxy group is coordinated. In the case of Citr@LaF<sub>3</sub> this difference is equal to 163 cm<sup>-1</sup>. This value is smaller than the corresponding value for the sodium citrate ion  $(172 \text{ cm}^{-1})$ , and, according to [7,8], we can conclude that the carboxy groups of citric acid are coordinated with the La(III) ions in the nanoparticle surface with the formation, mainly, of bridging or bidentate structures.



Table 3 shows the assignment of absorption bands in the IR spectra of glycine and Gly@LaF<sub>3</sub>. In the spectra of the modified samples the vibration bands were detected of amino, carboxy, and methylene groups, indicating the presence of glycine in the product. The COO<sup>-</sup> bands are shifted relative to the relevant bands of glycine zwitterions. This indicates the formation of bonds between carboxy group and the surface La(III) ions. The most striking evidence of this bonding is the disappearance in the IR spectrum of Gly@LaF<sub>3</sub> of the band at 506 cm<sup>-1</sup>, which belongs to the rotational vibrations of unbound carboxy group, and the appearance of the bands of the La–O bending vibrations at 585 cm<sup>-1</sup>. From comparison of the frequencies of asymmetric and symmetric stretching vibrations of carboxy groups  $\Delta = 223$  follows that the bond of the carboxy group to the La(III) ion is monodentate. This leads apparently to the formation on the surface of chelate complexes of LaF<sub>3</sub> nanoparticles

**Table 3.** The assignment of vibration frequencies  $(cm^{-1})$  in the IR spectra of glycine (Gly) and the lanthanum fluoride (Gly@LaF<sub>3</sub>) modified with glycine

Gly	Gly@LaF3	Assignment [9–13]
	3600-3300	$v_{OH}(H_2O)$
3167		$v_{s}(NH_{3}^{+})$
	1636	$\delta(H_2O)$
1618	1619	$\delta_{as}(NH_3^+)$
1593	1630	$v_{as}(COO^{-})$
1525, 1508	1523, 1508	$\delta_{s}(NH_{3}^{+})$
1444	1455	$\delta(CH_2)$
1414	1408	v <sub>s</sub> (COO <sup>-</sup> )
1335	1340	$\rho(CH_2)$
1133, 1114	1127	$\rho(\mathrm{NH}_3^+)$
1034	1036	v <sub>as</sub> (CCN)
912	908	$\rho(CH_2)$
894	867	v <sub>s</sub> CCN
699	669	$\rho_{\rm w}({\rm COO}^-)$
608		δ(COO <sup>-</sup> )
	585	$\delta(COO^{-}) + \delta(LaOC)$
	532	$\delta(CNH) + \delta(COH) + \delta(NCH)$
506		$\rho_r(COO^-)$
	419, 408	δ(LaF)

with simultaneous coordination of amino and carboxy groups:



At such coordination, there are no functional groups on the surface capable of entering into protolytic interactions with the components of the solution with changing the surface charge. As a consequence, the stability of such a system is almost independent of pH.

Fundamentally another situation is observed in the case of Citr@LaF<sub>3</sub>. As we have already shown earlier [2], the citric acid is attached to the EuF<sub>3</sub> surface by one carboxy group, and one of the two remaining groups is deprotonated. Similar fixation of citrate ions occurs in the case of the surface of gold nanoparticles [14]. At the contact with the surface lanthanide ions the citrate ions form a charged layer on the surface of the particle. Due to electrostatic repulsion, the similarly charged particles are less aggregating and do not precipitate. Lowering the medium pH by adding acid leads to complete deposition of particles at the pH 4.5–3. This is obviously a result of protonation of the ionized carboxy group, which removes the surface charge:



Repeated changes in pH of the system have no effect on the behavior of the system: at pH > 4.5 the particles become dispersed in solution, at pH < 4.5 they coagulate. This shows that the grafted citrate layer is rather stable. This feature can be used for the isolation of the resulting nanoparticles and their separation from impurities. In addition, the carboxy groups unbound with the nanoparticle surface can coordinate metal ions from solutions. At the interaction of a solution containing Cu<sup>2+</sup> ions with Citr@LaF<sub>3</sub> the particles are colored blue. The resulting bimetallic complexes are very strong: desorption of the copper

ions occurs only at the processing of the powder with the concentrated acid.

Thus, as a result of the study we demonstrated the possibility of obtaining the  $LaF_3$  nanoparticles with modified surface. At the interaction of organic acids with the surface La(III) ions complexes are formed with the composition and structure depending on the nature of the modifier: in the case of glycine they are chelates involving one N atom of the amino group and one O atom of the carboxy group; in the case of citric acid bridging or bidentate complexes are formed involving two O atoms of the carboxy group.

Polycarboxyic acids can be used to stabilize the resulting colloids because the carboxy groups unbound to the surface carry a negative charge. The particles obtained in the presence of citric acid can be repeatedly exposed to the processes of coagulation–dispersion by varying the pH of the system in the range from 3 to 8. These processes occur without destroying the grafted layer. This feature can be used for isolation and purification of nano-sized LaF<sub>3</sub> particles. The investigated method of modification can be used for the synthesis of colloids of other ionic compounds, in particular, of the lanthanide salts.

# **EXPERIMENTAL**

The X-ray phase analysis data were obtained on a DRON-3M instrument (Co $K_{\alpha}$  radiation,  $\lambda = 0.179021$  nm). The morphology of the synthesized samples was studied using a LEO912 AB OMEGA transmission electron microscope. This instrument was also used to obtain the X-ray photographs of modified samples by the Debye–Scherrer method. The particle size distribution was determined by dynamic light scattering on a Nanosizer Malven device. The IR spectra of the samples in KBr pellets were recorded on a Thermonicolet Fourier transform IR200 infrared spectrometer (resolution 4 cm<sup>-1</sup>, the number of scans 64).

Synthesis of LaF<sub>3</sub> nanoparticles. *Method 1.* 2 ml of LaCl<sub>3</sub> (0.0017 mol) was uniformly added dropwise at either 20 or 75°C to 25 ml of NaF (0.0051 mol) at continuous stirring. The formed LaF<sub>3</sub> particles were isolated in a centrifuge (8000 rpm), washed several times with water, and dried in air.

*Method 2.* To 100 ml of water at either 20 or  $75^{\circ}$ C at continuous stirring were added dropwise simultaneously 15 ml of solution of LaCl<sub>3</sub> (0.0017 mol) and

15 ml of solution of NaF (0.0051 mol). The formed LaF<sub>3</sub> particles were isolated in a centrifuge (8000 rpm), washed several times with water, and dried in air.

Synthesis of Citr@LaF<sub>3</sub> and Gly@LaF<sub>3</sub> nanoparticles. Synthesis was carried out by method 2 at  $75^{\circ}$ C, the solutions of reagents were added dropwise to 100 ml of a neutral (pH 7–8) solution of citric acid or aminoacetic acid (0.0017 mol).

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