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Sol-Gel Preparation and Magnetic Properties of Nanocrystalline Lanthanum Ferrite

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Abstract—$LaFeO_3$ nanoparticles (30–40 nm) have been prepared via the sol-gel method using polyvinyl alcohol as a stabilizer. Addition of polyvinyl alcohol results in the formation of smaller $LaFeO_3$ particles and decreases the temperature of transition into the single-phase product as compared with the samples prepared via precipitation with aqueous ammonia. Residual magnetization, magnetization at saturation, and coercive force of $LaFeO_3$ nanoparticles are monotonous decreasing functions of the nanopowder annealing temperature.

Keywords: nanocrystal, sol-gel synthesis, lanthanum ferrite, polyvinyl alcohol

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Crystalline ferrites of the perovskite type ABO_3 (A = rare earth element, Y, or La; B = Fe, Co, Ni, Mn, or Cr) and their solid solutions are of special interest among complex oxides due to their wide range of applications for the development of functional materials [1–8].

Chemical methods of ferrite-forming components homogenization provide for the uniformity and reactivity of the ferrite powders, and are therefore extremely important part of technology of ferromagnetic oxides production [9, 10]. In particular, the sol-gel preparation method is promising due to the lower annealing temperature (as compared with the solid phase synthesis) [11–13] along with using simple and cheap equipment.

$LaFeO_3$ nanocrystals with an average size of 100 nm can be prepared via co-precipitation of La(III) and Fe(III) hydroxides with aqueous ammonia at boiling, followed by annealing (950°C, 1 h) [14]. The prepared powders are usually highly agglomerated, which deteriorates the properties of the further produced materials. Various stabilizers, in particular, polyvinyl alcohol, are used in order to decrease the oxides synthesis temperature and to form smaller particles [15]. When using organic precursors, oxide products can be prepared by the burning-out method as well [16–18].

The influence of the stabilizer on the size and morphology of the formed nanoparticles has been studied in a number of works [15–17] (the latter two treating the $LaFeO_3$ nanoparticles); however, its effect on the magnetic properties of $LaFeO_3$ nanocrystals has not been systematically studied. To fill in this gap, in this work we investigated the magnetic properties of $LaFeO_3$ nanocrystals prepared via the sol-gel route in the presence of polyvinyl alcohol.

Thermogravimetric analysis of the sample prepared by co-precipitation of lanthanum(III) and iron(III) hydroxides in the presence of polyvinyl alcohol (Fig. 1), revealed a mass loss of 65.79%, much higher than that in the absence of polyvinyl alcohol, other conditions being the same (23% [14]).

The observed difference was due to the efficient interaction of La^{3+} and Fe^{3+} with polyvinyl alcohol resulting in the formation of relatively stable organometallic compounds decomposing upon heating. The constant mass of inorganic residue was reached at 600–650°C, whereas in the absence of polyvinyl alcohol mass loss was observed up to 950°C [14].

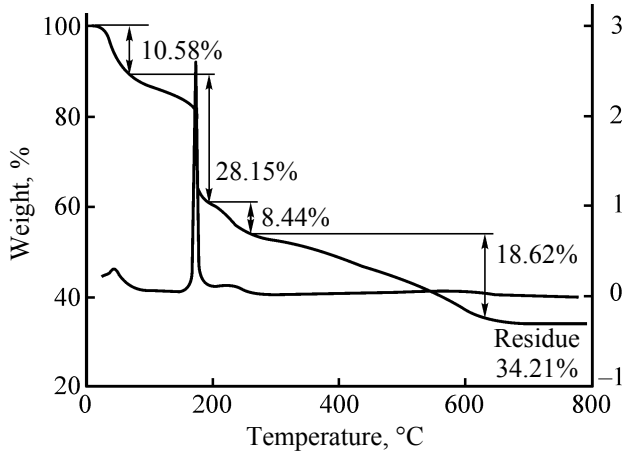

Fig. 1. Thermogravimetric analysis of $LaFeO_3$ prepared via the sol-gel route in the presence of polyvinyl alcohol.

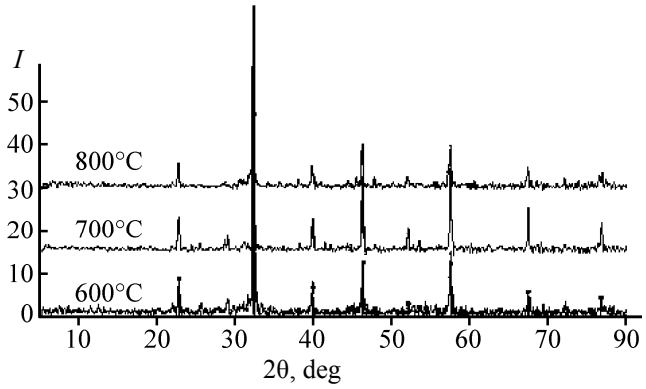

Fig. 2. X-ray diffraction patterns of the samples prepared via the sol-gel route in the presence of polyvinyl alcohol after 1 h of annealing. Annealing temperature is indicated near the corresponding curve. The curves are arbitrarily shifted vertically for clarity.

The most significant mass loss (about 40%) occurred up to 150–200°C, whereas at higher temperatures the mass decrease was slower. In the case of the sample prepared without polyvinyl alcohol, its heating in air as well as under inert atmosphere was accompanied mainly with endothermic effects (typical of desorption, evaporation, decarbonization, etc [14]). In the case of the sample prepared in the presence of polyvinyl alcohol, the specimen's heating was accompanied with exothermic oxidation of the alcohol and its decomposition products; that could be used to prepare $LaFeO_3$ nanoparticles using the gel burning method [16, 17].

According to atom absorption spectroscopy data, the composition of the prepared powders corresponded to $LaFeO_3$ (found La 56.37 wt %, Fe 22.93 wt %; calculated La 57.22 wt %, Fe 23.00 wt %).

Accounting for TGA results, $LaFeO_3$ was prepared by annealing at 600, 700, and 800°C for 1 h. X-ray diffraction studies revealed that the prepared samples were single-phase, with orthorhombic structures (Fig. 2).

The crystallite average size (size of coherent scattering area) of the $LaFeO_3$ powders was estimated from the X-ray diffraction line broadening (see table). In particular, increasing the annealing temperature from 600 to 800°C led to roughly two-fold larger crystallites formation.

Previously it was demonstrated that a reasonable estimation of the crystallite size from the diffraction lines broadening was possible only in combination with supplementary structural data, for instance, electron microscopy [19]. Electron microscope images of $LaFeO_3$ nanopowder prepared in this work via

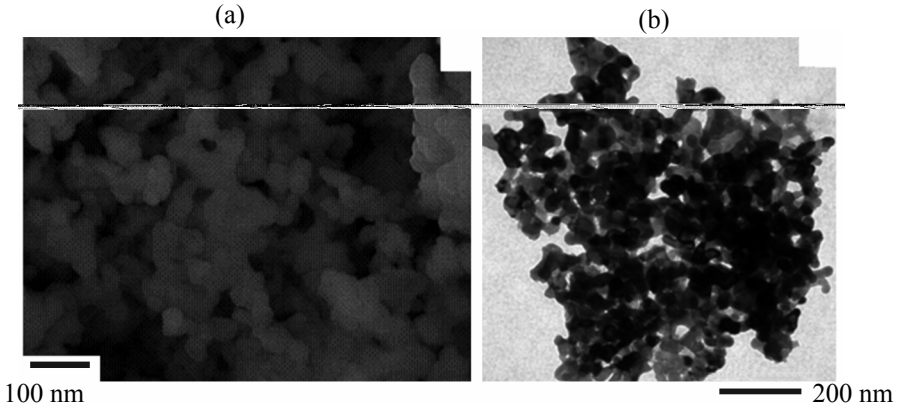

Fig. 3. Scanning (a) and transmission (b) electron microscopy images of $LaFeO_3$ powder prepared via the sol-gel route in the presence of polyvinyl alcohol (1 h annealing at 600ºC).

Properties of $LaFeO_3$ prepared in the presence of polyvinyl alcohol

Annealing temperature, °C	Crystallite size (Scherrer equation), nm	Residual magnetization at $H = 0$, A $m^2 kg^{-1}$	Magnetization at saturation, A $m^2 kg^{-1}$	Magnetization at the strongest field, A $m^2 kg^{-1}$	Coercive force, kA/m	Magnetic energy density, J/m^3
600	18	0.10	1.18	1.18	6.74	55.5
700	25	0.0183	0.253	0.253	3.95	0.000
800	30	0.00308	0.0123	0.0123	1.74	0.000

annealing at 600°C are shown in Fig. 3; the nanoparticles were isometric and slightly agglomerated, their size being 30–40 nm. At the same time, $LaFeO_3$ synthesis in the absence of polyvinyl alcohol led to particles larger than 100 nm [14]. The observed difference was likely due to suppressing the particles agglomeration by polyvinyl alcohol; in the absence of the polymer, particles agglomerates were observed in the images rather than the single particles.

Testing of the prepared materials with a vibration magnetometer at room temperature showed that all the determined parameters (in particular, residual magnetization M_r, magnetization at saturation M_s, and coercive force H_c) were monotonously decreasing functions of the annealing temperature (Fig. 4 and table). Probably that was related to the particles enlargement at higher annealing temperatures. For example, coercive force is known to be a function of the particle size [20]: $H_c = A/d + D$ with A and D being parameters depending on the active component concentration in the mixture, d being diameter of the active component nanocrystals.

To conclude, we prepared the isometric, non-agglomerated 30–40 nm $LaFeO_3$ particles via the sol-gel route in the presence of polyvinyl alcohol followed by annealing at 600–800°C. The addition of the polymer resulted in the formation of smaller particles and decreasing the temperature of the single-phase product formation (cf. [14]). The prepared $LaFeO_3$ nanopowders showed a narrow hysteresis loop, low coercive force and residual magnetization. Such combination of properties leads to the possibility of their application in the development of soft magnetic materials for magnetic field detectors and memory devices.

EXPERIMENTAL

Lanthanum ferrite was prepared by aqueous ammonia treatment of equimolar mixture of lanthanum(III) and iron(III) nitrates (both of "chemically pure" grade) in the presence of polyvinyl alcohol (M = 56700). In particular, 50 mL of aqueous solution of $Fe(NO_3)_3$ and $La(NO_3)_3$ (0.05 mol/L each) was added during stirring to 400 mL of boiling distilled water, and the solution was stirred during 15 min at 80–90°C. After that, 100 mL of polyvinyl alcohol solution in hot water was added, mass ratio of the polymer to sum of metal ions being 1 : 3 [16, 17]. The mixture was heated to 170–200°C, and the heating was continued till the formation of yellow-brown powder.

Thermogravimetric analysis of the powders was performed using the TGA Q500 V20.13 Build 39 analyzer (argon 99.998% atmosphere; heating rate 10 deg/min). Elemental analysis was performed by atom absorption spectroscopy (Shimadzu AA-6300). Phase composition of the samples was monitored by X-ray diffraction analysis (D8-Advance, CuK_α, λ = 1.54 Å). Crystallites size was determined using the Scherrer equation from the diffraction lines broaden-

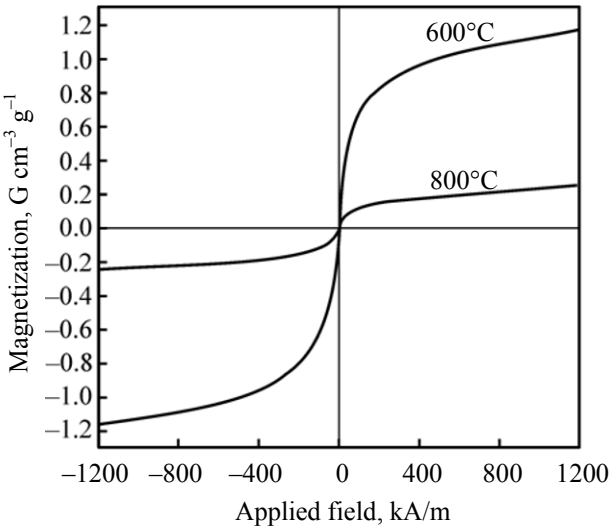

Fig. 4. Magnetization of $LaFeO_3$ nanocrystalline powder prepared via the sol-gel route in the presence of polyvinyl alcohol, as a function of the applied field. Annealing temperature is shown near the respective curve.

ing. Additionally, the shape and size of the nanoparticles were determined by transmission (JEM-1400) and scanning (S-4800) electron microscopy. The magnetic properties of the materials were tested with the Microsene EV11 vibration magnetometer at room temperature.

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