Synthesis of solid solutions Ln-Fe-O using aerosol spray pyrolysis method

Anastasia E. Goldt[1,2], Albert G. Nasibulin[1,3]

[1] Laboratory of Nanomaterials, Skolkovo Institute of Science and Technology, Moscow, 143026, Russia
[2] Department of Materials Science Lomonosov Moscow State University, Moscow, 119991, Russia
[3] Department of Applied Physics, Aalto University, Finland
Keywords: spray pyrolysis, perovskite, $LnMnO_3$
Presenting author email: a.goldt@skoltech.ru

Rare-earth orthoferrites with the composition of $LnFeO_3$ (Ln-rare earth element) demonstrate unique physical and chemical properties for various applications, for instance, gas separators, sensor and magneto-optic materials, *etc.* $LnFeO_3$ (Ln = La, Gd, Pr) have distorted orthorhombic perovskite structure, where FeO_6 as a rotary tilted polyhedron fills the empty space left around the Ln group. There is a mixed valence state of Fe^{2+}/Fe^{3+} originated from the 3d iron ions in $LnFeO_3$ resulted from an anion deficiency, making $LnFeO_3$ material with prominent electrical and magnetic properties.

Perovskites could be synthesized by simply heating the corresponding metal oxides in a stoichiometric ratio. The main difficulty in obtaining single-phase $LnFeO_3$ is the presence of undesired phases of $Ln_3Fe_5O_{12}$ and Fe_3O_4. Moreover, the garnet phase ($Ln_3Fe_5O_{12}$) is thermodynamically more stable than $LnFeO_3$.

One important problem of the perovskite phase synthesis is related to high processing temperature and therefore to high energy consumption during the synthesis. For increasing the chemical reaction rate and decreasing the temperature of the synthesis, a various routes of soft-chemistry (for example glycine-nitrate combustion reaction, sol-gel, co-precipitation method, hydrothermal treatment, *etc.*) are usually used.

In the present work, we utilized an ultrasonic aerosol spray pyrolysis method to prepare micron-sized granules. This method is an effective technique to prepare particles with a wide range of compositions of controllable size from a few hundred nanometers to a micrometer range. It is worth nothing that the method allowed us to synthesize a product with homogeneous composition, easy controllability, and short production times.

The precursor solutions were prepared by dissolving a stoichiometric amount of nitrate salts ($La(NO_3)_3/Fe(NO_3)_3$; $Gd(NO_3)_3/Fe(NO_3)_3$; $Pr(NO_3)_3/Fe(NO_3)_3$) in distilled water. The nitrate solutions were atomized using an ultrasonic nebulizer with a resonant frequency of 1.7 MHz.

The aerosol flow was introduced into the quartz reactor at 650 - 850 ºC by nitrogen flow. The obtained particles were collected downstream of the furnace on a filter. The flow rate of nitrogen used as a carrier gas was varied from 1 to 5 l/min, which corresponded to the residence time down to 3 seconds. The number concertation of particles depending on the conditions was varied and controlled with a water based a TSI SMPS system.

SEM image of nanocrystalline particles (La-Fe-O) prepared by ASP method is presented in Figure. Particles are microspheres from 150 to 400 nm in the diameter.

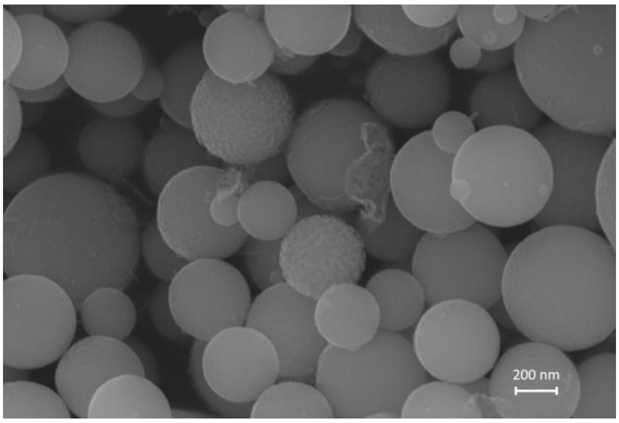

Figure. Particles produced at 700 ºC

Phase transitions in the system Ln-Fe-O (Ln-La, Pr, Gd) were analyzed in a wide temperature range (400-600 ºC) to obtain single-phase samples.

It was shown that our approach allowed us to obtain single-phase $LnFeO_3$ with a submicron grain size and spherical micromorphology. The applications of the particles for various markers have been tested.

Vinila Bedekar, O.D. Jayakumar, J. Manjanna A.K. Tyagi (2006) *Materials Letters* **62** 3793–3795.

Jun Yanga, Runsheng Li, Junyi Zhou, Xiaoci Li, Yuanming Zhang, Yulin Long, Yongwang Li (2010) *Journal of Alloys and Compounds.* **508 (2)**, 301-308.

M Rajendran, A.K Bhattacharya (2004) *ECerS.* **24 (1)**, 111-117.