SYNTHESIS OF FINE-DISPERSED OXIDES $La_2Zr_2O_7$, $La_2Hf_2O_7$, $Gd_2Zr_2O_7$, $Gd_2Hf_2O_7$

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Abstract

Synthesis of $La_2Zr_2O_7$, $La_2Hf_2O_7$, $Gd_2Zr_2O_7$, $Gd_2Hf_2O_7$ was carried by citrate method. Laser mass spectrometric analysis allowed us to determine the quantitative ratio between the metals in the synthesized materials, which corresponds to a given one. X-ray diffraction analysis confirmed the formation of single phase products with a cubic crystal lattice. The morphology of the compounds was investigated using scanning electron microscopy. It was established that the samples are porous skeletons in the form of foam with thin walls, which explains their low bulk density. Determined values of specific surface area were in the range from 20 to 37 m^2/g. Sintering process was investigated using tablets, obtained by pressing of the synthesized powders. The samples were heat treated in air at temperatures of 800, 900 and 1000°C. X-ray diffraction analysis revealed the growth of grain size.

1 Introduction

Creating materials that can operate continuously at high temperatures (above 1800-2000°C), is an important area of modern chemistry. Obtained of nanosized refractory oxides is an important and urgent task to solve the problems of modern materials. Such characteristics of substances, as refractoriness, low thermal conductivity, phase stability and, consequently, the possibility of using this substances in large temperature differentials are the main and important both individually and in combination. Zirconates and hafnates of lanthanides with the general formula $A_2B_2O_7$, having a cubic pyrochlore structure, due to the properties of their structure, chemical passivity, thermal stability, the absence of phase transitions up to the melting temperature (mostly > 2000ºC) are promising materials for refractory oxide ceramic coatings as well as a refractory oxide matrix of high-temperature composite materials. The use of lanthanide zirconates and hafnates for these purposes in a highly dispersed state has some obvious advantages, in particular, the possibility of obtaining uniform layers with controlled thickness and lowering the sintering temperature of the oxide matrix composites for units for energy production, working under extreme conditions - at high temperatures and in high-enthalpy gas streams.

Now there is a high need for the development of modern high-efficiency methods of obtaining of zirconates and hafnates of lanthanides, in particular, lanthanum and gadolinium, which open and complete the series of compounds of the pyrochlore structure $A_2B_2O_7$ (although for compounds $A_2Hf_2O_7$ there is evidence that the structure of pyrochlore persists to $Tb_2Hf_2O_7$),

not only with given the elemental composition (strict adherence to the stoichiometric ratio of metal atoms, reduced content of impurity components), but with a developed surface, which is important for the development of temperature and chemically stable carriers for catalysts, materials for chemicalsensorics. In this paper, we propose to use the citrate method [1-3], which is also known in the literature as Pechini method [2], for the preparation of compounds.
Practical significance have special studies of the process of sintering of synthesized powders and tablets of highly refractory compounds, which allow to predict the behavior of the substances during obtaining of ceramic products, and also estimate possible obtaining conditions of ceramics based on them.
The purpose of work is the synthesis of nanocrystalline zirconates and hafnates of lanthanum and gadolinium ($La_2Zr_2O_7$, $La_2Hf_2O_7$, $Gd_2Zr_2O_7$, $Gd_2Hf_2O_7$) with pyrochlore structure using the citrate method, their identification, investigation of the morphology and dispersion, as well as studying thermal stability and sintering processes.

An Experimental

1.1 Synthesis $La_2Zr_2O_7$, $La_2Hf_2O_7$, $Gd_2Zr_2O_7$, $Gd_2Hf_2O_7$

In order to obtain highly dispersed powders of zirconates and hafnates of lanthanum and gadolinium inorganic metal salts (hafnium or zirconium oxide dichloride octahydrate, gadolinium nitrate hexahydrate or lanthanum oxide) in stoichiometric ratios were dissolved in water with the addition of concentrated nitric acid, were subjected to heat treatment in boiling solution. Next citric acid and ethylene glycol were added to the system, followed by neutralization with a solution of ammonia hydrate.
After that we performed evaporation until a viscous solution, following further heating to a temperature of 250-350ºC and initiating of an exothermic self-propagating synthesis. The resulting product was a grayish powder with dendrite-like structure, to remove residual carbon, it was calcined at a temperature of 650-700ºC for 1-2.5 hours, resulting the bulk powders dendrite-like morphology (Fig. 1), low bulk density (for example, for $La_2Zr_2O_7$ it was 0.02 g/cm^3). After annealing the yield of compounds was 98-99%.
Laser mass spectrometric analysis (EMAL-2) allowed us to determine the quantitative ratio between the metals in the synthesized materials, which corresponds to a given one (deviation of ratio Ln: Zr (Hf) in all cases is within the homogeneity regions of the compounds and does not exceed 2%). The total content of «coloring» admixtures is less than 0.5 at.% for all the synthesized compounds.
XRD analysis revealed that, the cubic phases of zirconate and hafnate of gadolinium formed in the synthesis, and samples of zirconate and hafnate of lanthanum were X-ray amorphous (see Fig. 2). Mean average crystallite size for $Gd_2Zr_2O_7$ and $Gd_2Hf_2O_7$, which amounted to 6 and 5 nm, respectively was calculated by the Scherer's formula.
The specific surface area of powders was determined by BET method - nitrogen adsorption at 77 K on the adsorption weight set (IPCE RAS). The obtained values ranged from 20-21 (for $La_2Zr_2O_7$ and $La_2Hf_2O_7$) to 30-37 (for $Gd_2Hf_2O_7$ and $Gd_2Zr_2O_7$) m^2/g.
Using DTA-TGA-DSC method (combined TGA/DSC/DTA analyzer SDT Q-600) we studied the thermal behavior of the synthesized product in the temperature range 20-1200ºC under flow of air- Fig. 3. At these temperatures the thermograms were found to have no thermal effects associated with phase transitions. At the same time weight lose is 4-6% (mainly at temperatures less than 400ºC and in the range of 800-950ºC), which may be due to desorption of surface gases and burnout of residual carbon (a slight exotherm with a maximum of 900-920ºC) during the disclosure of closed porosity while heating of the powders to temperatures of crystallization and ordering of cubic pyrochlore phase.

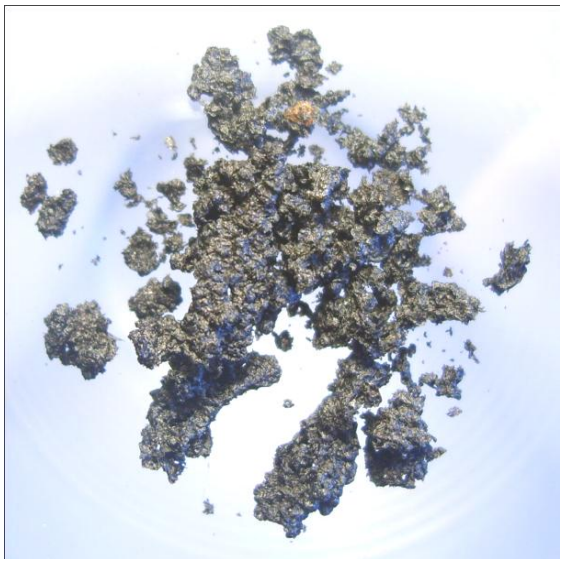

Figure 1. The appearance of the $La_2Hf_2O_7$ powder before removal of the residual carbon

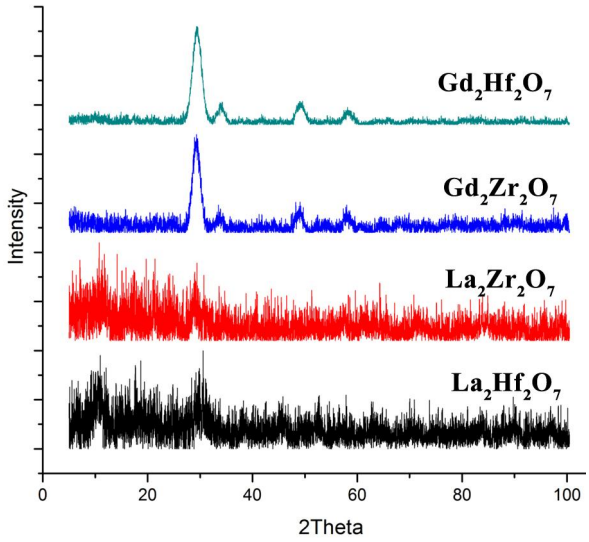

Figure 2. XRD-patterns of the products after removal of carbon excess

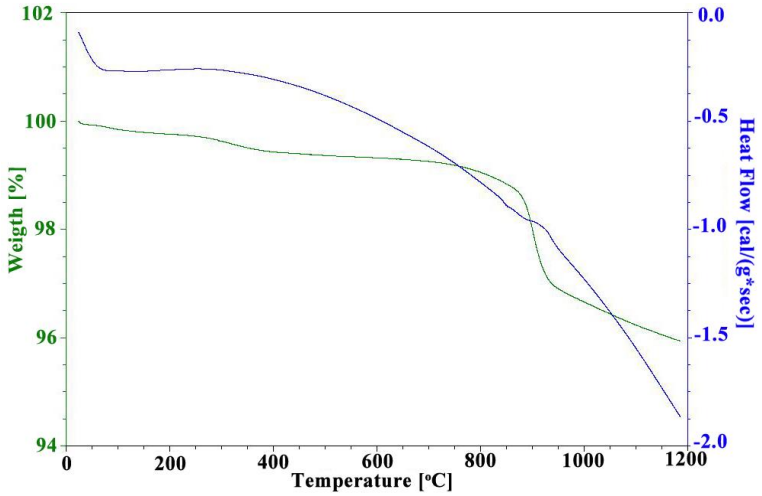

Figure 3. Thermograms of $La_2Hf_2O_7$ powder after removal of carbon excess

The study of surface morphology of oxides by scanning electron microscopy (three-beam workstation NVision 40, Carl Zeiss,) indicates that the powders are a complex form of the films with a hidden porosity and thickness from several tens to hundreds of nanometers (Fig. 4).

1.2 Sintering of the obtained powders

The powders of zirconates and hafnates of lanthanum and gadolinium were pressed in tablets (pressure of 64 atm/cm^2) and sintered at temperatures of 800, 900 and 1000ºC for 1, 2 and 4 hours. After that the tablets were subjected to grinding.

For all samples, which were heat-treated, even at the lowest temperature and time, we can see the formation of the cubic phase with the structure of pyrochlore, although IR spectroscopy showed that a complete ordering of the structure occurs only as a result of exposure of tablets at 1000ºC - there are characteristic absorption bands in the range 400-650 cm^{-1} [4].

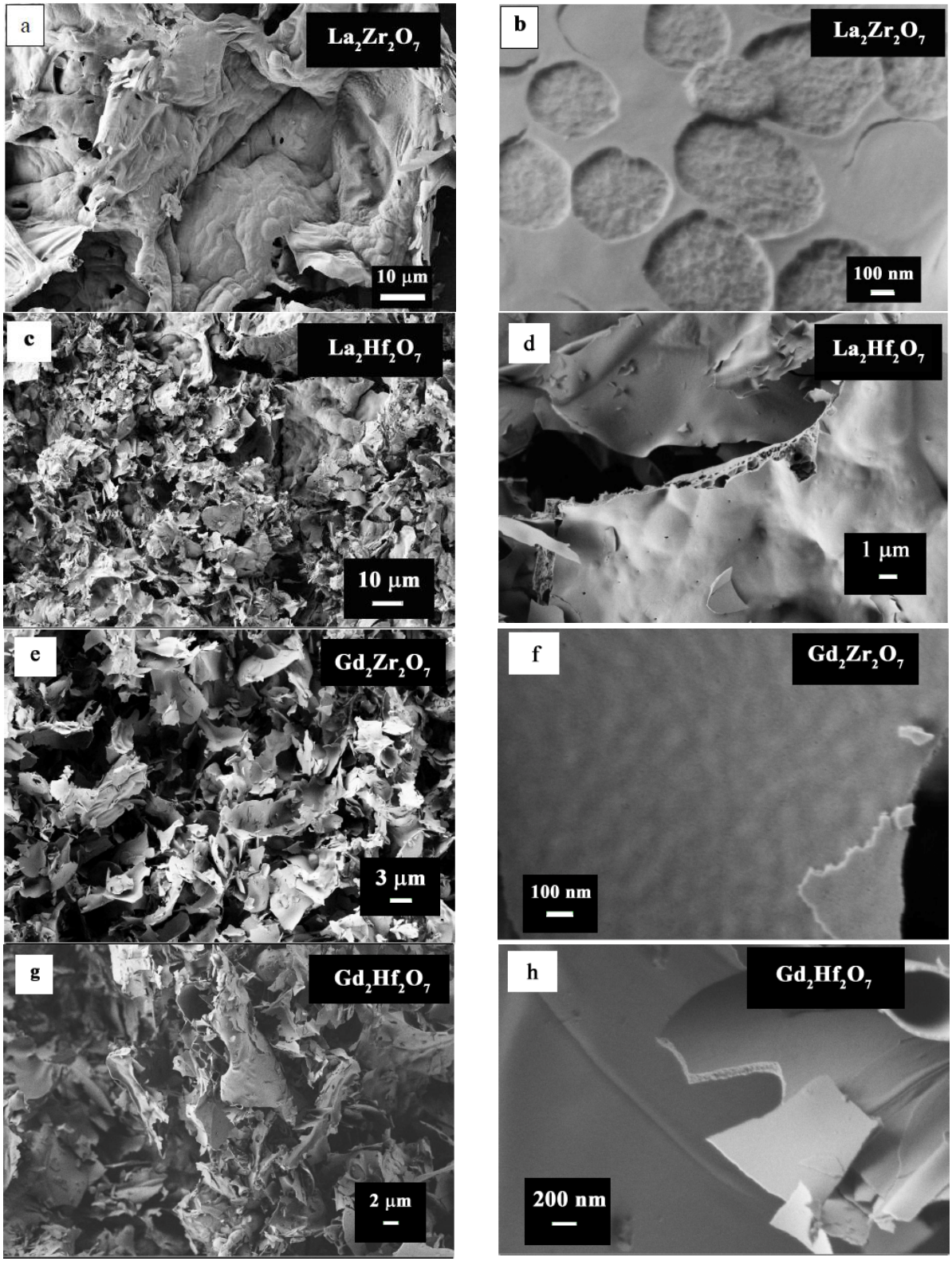

Figure 4. Microstructure of product powders after the removal of carbon

X-ray analysis of $Gd_2Hf_2O_7$ sample, sintered under these conditions shows an increase in the average crystallite size with increasing sintering temperature and time. The average size of crystallites during calcination at 800ºC for 1 hour is ~ 5 nm, and at 1000ºC for 4 hours - 19 nm, while coarsening of the particles depends more on temperature than on the time of the process. For the zirconate of gadolinium $Gd_2Zr_2O_7$ the average crystallite size is greatly

increased from 7 (sintering temperature 800ºC, exposure - 1 h) to 103 nm (sintering temperature 1000ºC, exposure - 4 hours). An increase in the crystallite size also were revealed for zirconate and hafnate of lanthanum: $La_2Zr_2O_7$ – from 17 (sintering temperature 800ºC, exposure - 1 h) to 38 nm (sintering temperature 1000ºC, exposure 4 h); $La_2Hf_2O_7$ - from 38 (the sintering temperature 800ºC, exposure - 1 h) to 53 nm (sintering temperature 1000ºC, exposure - 4 h).

The processes of sintering of metal oxides were also investigated by measuring of the specific surface area. It was revealed that for the compounds of gadolinium the surface area (7.9 m^2/g) are almost independent from the exposure time at 1000ºC. At the time, for the compounds of lanthanum at the sintering temperature 800ºC there is a decrease of specific surface area, but at the sintering temperature of 900ºC there is the growth of S, which may be associated with the processes of opening previously closed porosity due to shrinkage of some samples. Further, the specific surface area begins to reduce again when the sintering temperature rises to 1000ºC.

Scanning electron microscopy allows to suggest that the sintering process depends strongly on the compound - Fig. 5. For zirconate and hafnate of lanthanum the size of particles obtained by sintering at 1000ºC for 4 hours is almost the same. The resulting size of aggregates of particles, identified by SEM for the above-mentioned heat treatment conditions of $Gd_2Zr_2O_7$ tablet, was 80-100 nm, there were particles with sizes up to 200-220 nm. The average particle size of gadolinium hafnate $Gd_2Hf_2O_7$ was significantly smaller - 20-30 nm.

Also research work on the process of enlargement of the particles (without pressing) at high temperatures - subsequent double heating to a temperature of 1200ºC in a DTA experiment (in an air flow of 100 ml/min, heating rate of 20º/minute) was carried out.

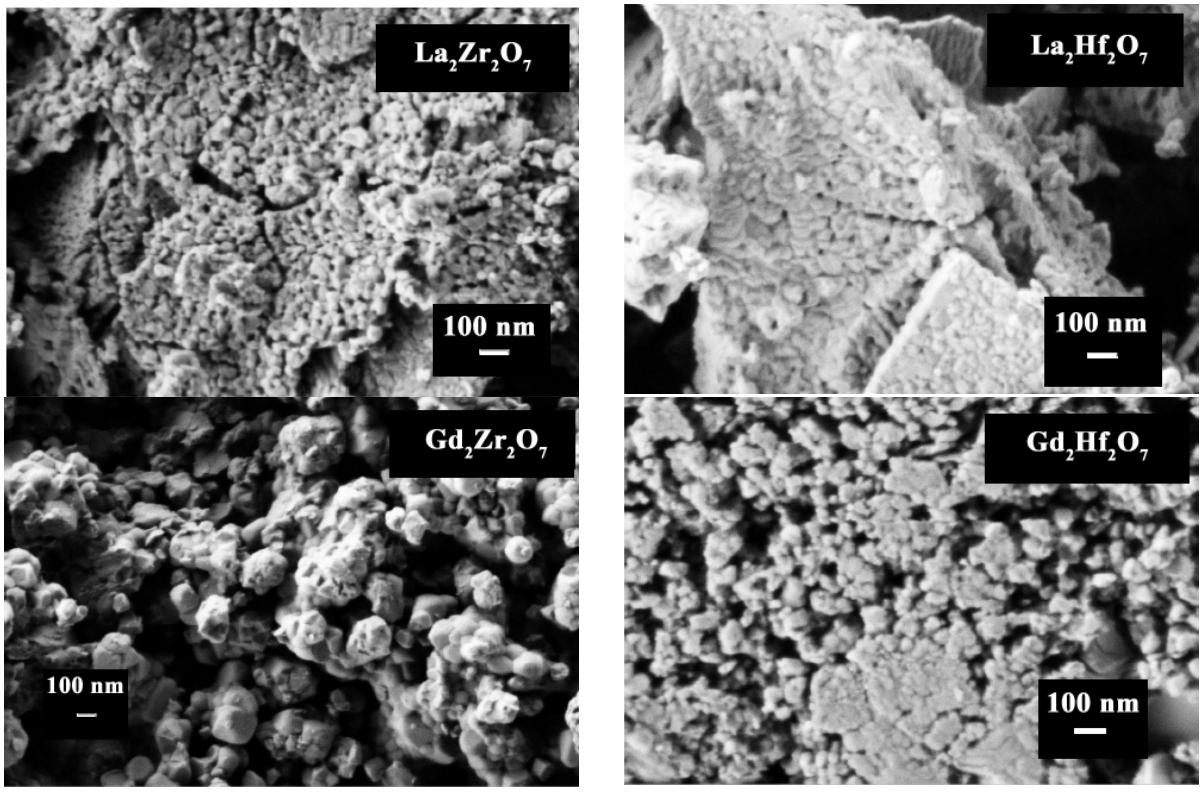

Figure 5. The microstructure of the samples of $La_2Zr_2O_7$, $La_2Hf_2O_7$, $Gd_2Zr_2O_7$, $Gd_2Hf_2O_7$ after sintering at 1000ºC for 4 hours (tablets)

SEM revealed the formation of delicate mesh structures as a result of sintering of weakly aggregated powder with low bulk density - Fig. 6. The structures were formed from particles

with an average size of 30-40 nm, including zirconate of gadolinium, which were sintered the best.

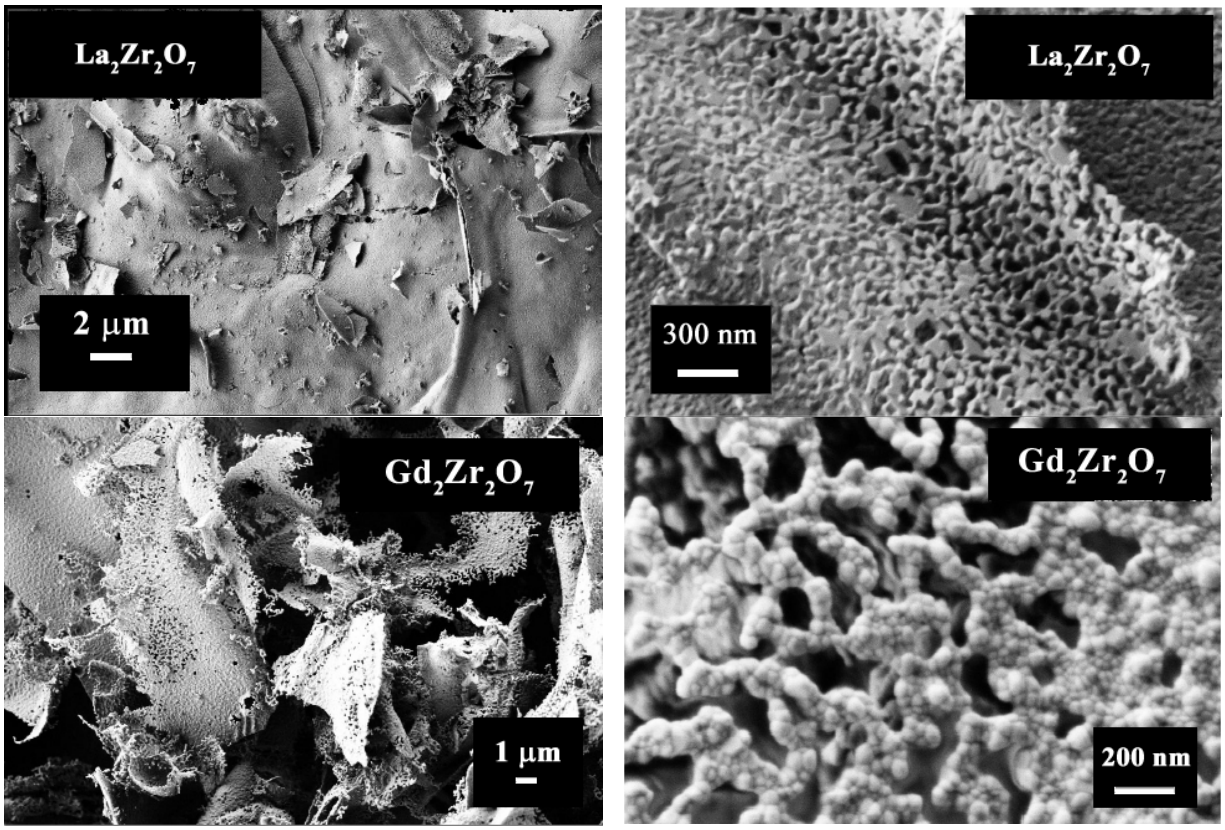

Figure 6. The morphology of powders of $La_2Zr_2O_7$ and $Gd_2Zr_2O_7$ after double heating up to 1200ºC in air

Conclusion

In this work the fast, high-performance method for obtaining of highly dispersed nanocrystalline metal oxide $Gd_2Hf_2O_7$, $Gd_2Zr_2O_7$, $La_2Hf_2O_7$ and $La_2Zr_2O_7$ with pyrochlore structure and «coloring» impurities content less than 0.5 at.%. was developed. Their phase composition, morphology and dispersion were determined, thermal behavior was studied in the temperature range 20-1200ºC using the method of DTA/DSC/DTG.

The process of sintering of the obtained compounds in the form of tablets or powder with low bulk density was investigated, the relationship between the crystallite size, specific surface area and heat treatment temperature and time was obtained.

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