Mechanism of formation of lanthanum aluminate crystals in supercritical water fluid.

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In this paper the results of investigations of phase change of precursor structure during formation of fine crystalline undoped lanthanum aluminate and doped with cerium in supercritical water are represented.
The products of synthesis at each stage were investigated by methods of X-ray diffractometry, and electron microscopy. The lanthanum aluminate synthesis was carried out in two stages in water vapor medium from mechanical mixtures of lanthanum oxide and aluminum hydroxide. At first, this mixture was treated by subcritical water vapor (T<374°C) and then by supercritical water fluid (T=400°C, P=22 MPa). After treatment of the mixture of starting materials by subcritical water vapor the mixture of two phases: crystals of lanthanum hydroxide and roentgen-amorphous disordered AlOOH, were arisen. At usage of the additive of cerium nitrate the hexagonal oblong prismatic crystals of lanthanum hydroxide, corresponding to hexagonal syngony their structure, will be formed. Without cerium in the same conditions the ill-formed cubic crystals of lanthanum hydroxide, maintaining a habitus of a starting material - lanthanum oxide of cubic syngony will be obtained. During treatment of supercritical fluid the diffusion of aluminum ions in crystals of lanthanum hydroxide occurs. After a time of treatment by supercritical water fluid, in both cases the submicron cubic crystals of lanthanum aluminate according to cubic habitus were formed.

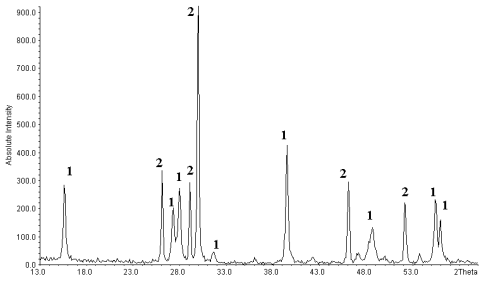
INTRODUCTION

Lanthanum aluminate is one of the important materials widely used in electronic industry. It is used at the fabrication of high frequency capacitors, magnetohydrodynamic generators, as well as raw material for production of superconductor [1-5]. The preparation of $LaAlO_3$ by solid state reaction method from mixture of aluminium oxide (Al_2O_3) with lanthanum oxide (La_2O_3) at high temperatures is used mostly [6 -8]. $LaAlO_3$ powder has also been synthesized by aqueous co-precipitation method with subsequent air calcination [9, 10]. Lanthanum aluminate has been also obtained by combustion synthesis process using nitrate salts of lanthanum and aluminium as cation precursors and urea as the fuel [11].
Earlier, authors of this paper designed method of lanthanum aluminate preparation by treatment of a mixture of aluminium hydroxide and lanthanum hydroxide by supercritical water fluid (SCWF) at 400 °C (P_{H2O}=22 MPa) during 18 –24 hours [12, 13]. In water vapor the lanthanum aluminate synthesis was carried out in two stages: from the beginning at 230 °C, P_{H2O}=2. 5 MPa and then at 400 °C (P_{H2O}=22 MPa). During the first stage the product synthesis was the mixture of lanthanum hydroxide and disordered boehmite. At the second stage was the lanthanum aluminate was formed. This method of the synthesis allows to producing the pure or doped lanthanum aluminate the crystal sizes from 0.2 to 6.0 μm [14].

In this paper the results of investigations of mechanism of transformation of precursor structure during formation of fine-crystalline lanthanum aluminate in SCWF are given.

MATERIALS AND METHDS

As starting material the mixture of lanthanum oxide with aluminum hydroxide was used. As have shown X-ray diffraction investigations, lanthanum oxide in ambient air is hydrated and has transformed to hydroxide of lanthanum $La(OH)_3$ with an impurity of oxyhydroxide AlOOH (Figure 1). The lanthanum aluminate synthesis was carried out in laboratory autoclaves of 18 cm^3. The mixture of lanthanum oxide (rather - hydroxide of lanthanum) with aluminum hydroxide was placed into container in autoclaves. The synthesis was carried out in two stages in water vapor medium. At first, the precursor mixture was treated by water vapor at 200 °C (P_{H2O}=1.5 MPa) during 20 hours, and then in water fluid at 400 °C (P_{H2O}=22 MPa) during 20 –72 hours. Necessary water vapor pressure was created in the autoclave by heated water, which was poured between the walls of the autoclave and the container with the raw material. In others cases the treatment of precursor mixture was carried out only at 400°C and P_{H2O}=22 MPa. For doping of lanthanum aluminate the same amount of the dopant, cerium nitrate, was placed into the container with the dry precursor mixture.
The synthesized products were explored by methods X-ray (diffractometer DRON-3M and diffractometer "STOE stad1p" in filtered Cu-*K*α radiation).
Habitus and of the crystals sizes was determined from the analysis of the SEM and TEM images by the microscopy "Cam Scan Series 2" and Transmission Electron Microscope Jeol JEM -1011.



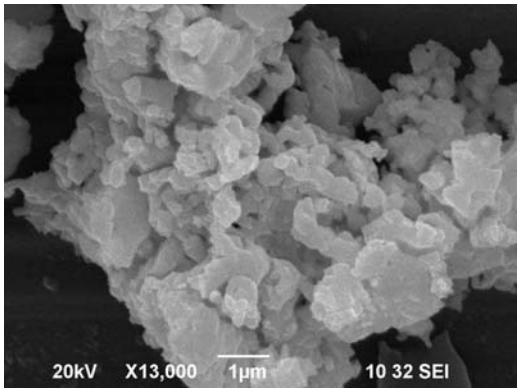


Figure 1. Difractogram and SEM-photo of raw material, hydrated Al_2O_3:1 - AlOOH; 2 – $Al(OH)_3$.

RESULTS

The investigations had shown that already during the treatment of the starting mixture ($Al(OH)_3$ and hydrated Al_2O_3 with additive of cerium nitrate) by subcritical water vapor the mixture of two phases, fine crystals of lanthanum hydroxide and roentgen-amorphous disordered boehmite (AlOOH) were arisen. At increasing the treatment temperature to 400°C the lanthanum aluminate is formed, however X-Ray analysis reveals still a small impurity of residuary lanthanum hydroxide and lanthanum oxyhydroxide (**Figure 2**).

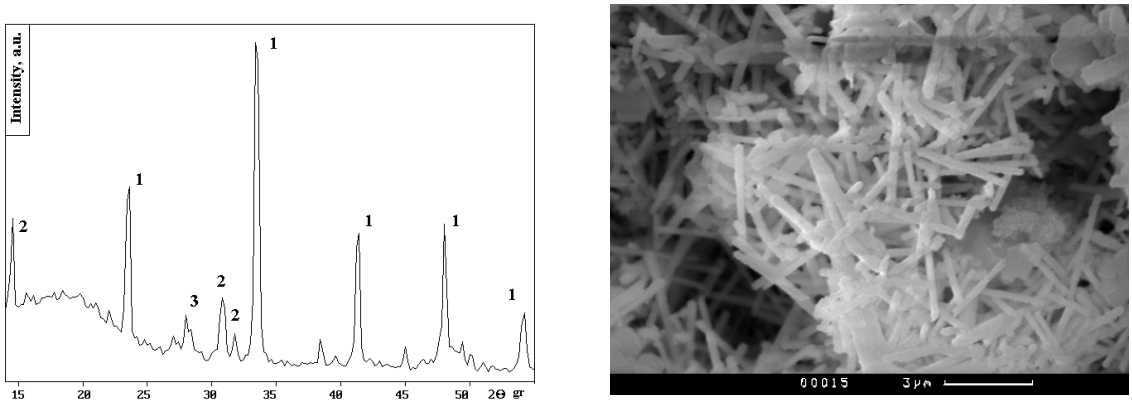


Figure 2. Difractogram and SEM-photo of products the treatment by water vapor of the starting mixture ($Al(OH)_3$ and $La(OH)_3$ with additive of cerium nitrate 1%) at P_{H2O}=22 MPa and T=200°C (22 h), then T=400°C (48 h); 1 – $LaAlO_3$, 2 – LaOOH, 3 – $La(OH)_3$.

It is significant that in presence of cerium nitrate lanthanum hydroxide and forming lanthanum aluminate have habitus of an oblong hexagonal prism, whereas the X-Ray studies reveal that lanthanum aluminate has a pseudocubic structure. The uncharacteristic shape of lanthanum aluminate crystals, having pseudocubic structure, can be caused by habitus of the precursor ($La(OH)_3$). Really, habitus of $La(OH)_3$, obtained from hydrated Al_2O_3 (raw material) with additive Ce (1%) at 400°C under P_{H2O}=21 MPa for 24 hours, represents oblong hexagonal prism (**Figure3**).

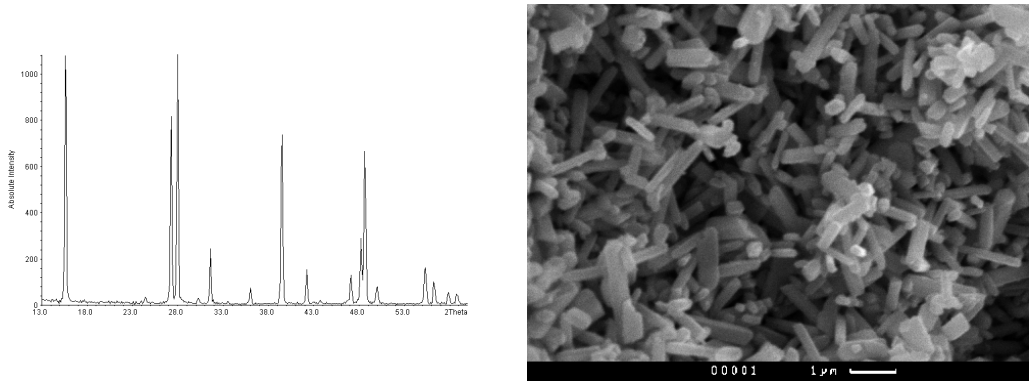
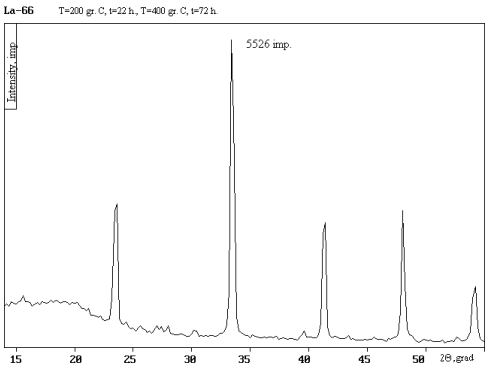


Figure 3. Difractogram and SEM-photo of $La(OH)_3$, obtained from hydrated Al_2O_3 (raw material) with additive Ce (1%) at 400°C under P_{H2O}=21 MPa for 24 hours.

In the same conditions, but without the additive of nitrate cerium, $LaAlO_3$ with ill-formed crystals close to cubic shape is arisen (**Figure 4**). The similar shape $La(OH)_3$ crystals have in initial phase (**Figure 1**) as well as after treatment by SCWF (without Ce) (**Figures 5 and 6**). From these facts it transpires that crystals morphology of La-containing products at all stages of process of $LaAlO_3$ formation from a mixture of hydrated aluminum oxide with hydroxide of aluminium without cerium is determined by morphology of an initial state of starting aluminum oxide - pseudo-cubic shape.



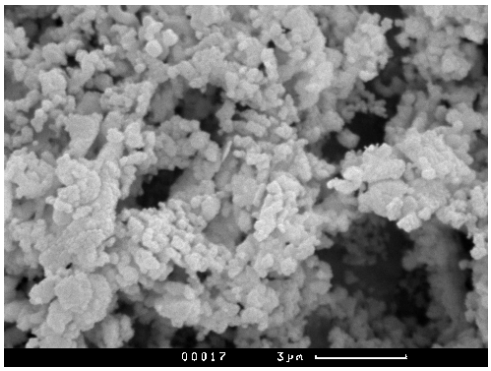
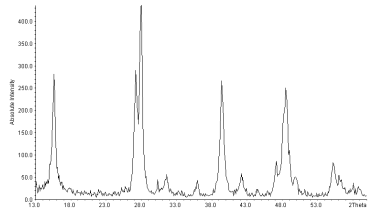


Figure 4. Difractogram and SEM-photo of $LaAlO_3$ obtaining from hydrated Al_2O_3 (without Ce) at 200°C (22 h), then T=400°C (72 h) under P_{H2O}=21 MPa.



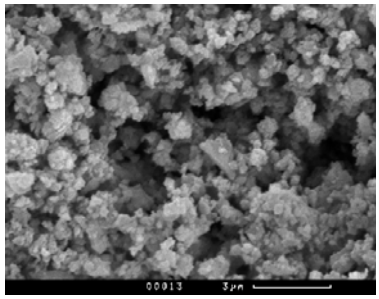


Figure 5. Difractogram and SEM-photo of $La(OH)_3$ after treatment
by SCWF (without Ce) at T=400°C, P_{H2O}=22 MPa =21 MPa, for 24 hours.

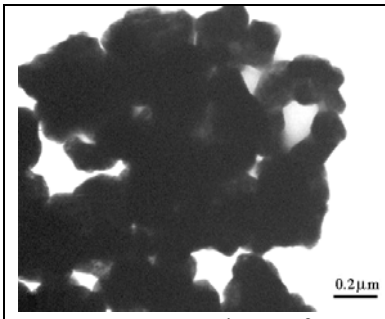


Figure 6. TEM-photo of $La(OH)_3$ after treatment by SCWF at 400°C, 21MPa,72 h.

The effect of SCWF on the needle-shaped $LaAlO_3$ crystals results in their intergrowth and to increasing of their size and then to the destruction with formation of fine crystals cubiform (**Figures 7 -10**).

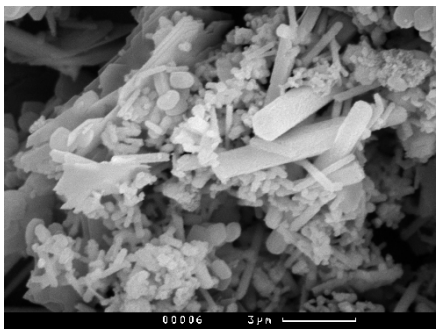


Figure 7. SEM-photo of LaAlO3 crystals synthesized at T=200°C, 22h, then T=400°C, P_{H2O}=22 MPa, 48 h, 0.5% Ce.

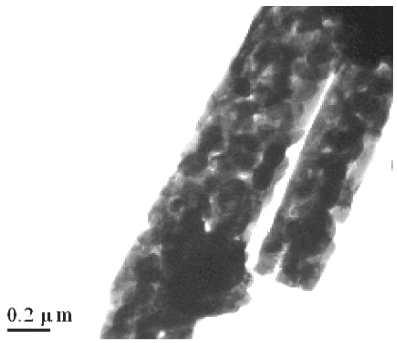


Figure 8. TEM-photo of LaAlO3 crystals synthesized at T=200°C, 22h, then T=400°C, P_{H2O}=22 MPa, 48 h, 1% Ce.

Thus, in medium of supercritical fluid (with Ce) inward diffusion of aluminum ions in prismatic crystals of lanthanum hydroxide occurs and the hexagonal oblong prismatic crystals

of lanthanum aluminate were formed, and without Ce, ill-formed cubic crystals of lanthanum aluminate were arisen. After a time, in both cases submicron cubic crystals of lanthanum aluminate according to cubic syngony were obtained.

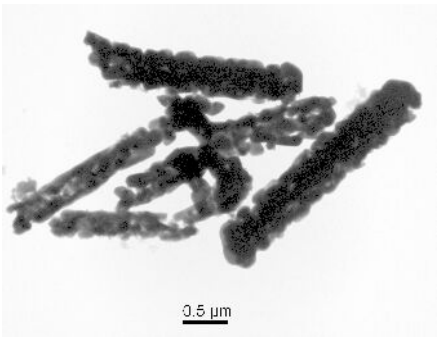


Figure 9. TEM-photo of $LaAlO_3$ crystals synthesized at T=200°C, 22h, then T=400°C, 48h, 1% Ce.

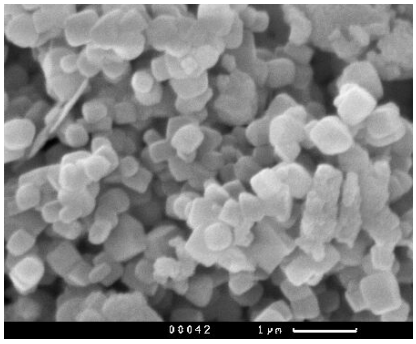


Figure 10. SEM-photo of $LaAlO_3$ synthesized at T=200°C, 22h, then T=400°C, 72h, 1% Ce.

Thus, it is shown, that the process of $LaAlO_3$ formation and morphology of intermediate products depend on presence of the doping additives, in this case from the additive of cerium nitrate.

CONCLUSION

In the authors' opinion that the most interesting fact in obtained results of investigations of the mechanism of crystals formation undoped and doped $LaAlO_3$ from an mixture of hydroxides of lanthanum and aluminium under activity of water fluid is the manifestation of a inconsistency between a habitus and syngony of crystals structure.

The peculiarity of solid-phase processes in water vapor, especially in a supercritical water fluid, consist in increase of mobility of a crystal lattice of reagents due to bonds opening during quasi-equilibrium processes of hydroxylation - dehydroxylation, therefore the bonds reorientation is put into effect [15]. The process of the formation of a new phase was started from the origins of multiple nucleuses in all volume of precursor. So, during treatment of the starting mixture ($Al(OH)_3$ and $La(OH)_3$ with additive of cerium nitrate by supercritical water fluid at 400 °C (P=22 MPa) during 20 - 24 hours a diffusion of aluminium into channels of structure of lanthanum hydroxide with formation nanocrystals of lanthanum aluminate in all volume of crystals of lanthanum hydroxide occurs, but for all the prismatic crystal shape of lanthanum hydroxide was remained (**Figure 8**). Then this crystal breaks up to fine crystals of pseudo-cubic shape (**Figures 9, 10**).

Due attention should be given to the fact of a discordance of a real habitus of crystals and a syngony of their structure. This strange phenomenon presumably was stipulated by the synchronous development of the structure formation of a new phase in all volume of a precursor crystal with conservation of its shape.

The investigation of the influence of a doping on morphological properties of crystals, first of all on their real habitus, has allowed determining optimal conditions of obtaining of LaAlO3 crystals with the various sizes and various shapes.

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