SYNTHETIC MAGNESIUM SPINEL - RAW MATERIAL FOR OPTICAL CERAMICS

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ABSTRACT
In this report are given the results of a study of the formation of fine -crystalline magnesium aluminate ($MgAl_2O_4$) from magnesium oxide and aluminum hydroxide or oxyhydroxide (boehmite) in medium of supercritical water fluid at temperature 380 - 400oC, and under pressure of water fluid 20 - 23 MPa. By varying the synthesis conditions and composition of supercritical water fluid, the particle size (from 20 nm to 5 microns) and the shape of the synthesized spinel (from spherical to bipyramidal) regulated. Synthesized by this method the fine-crystalline magnesium spinel proved as good starting material for the production of ceramics, in particular, for optical transparent ceramics. From this material were obtained transparent ceramics with transmission coefficient up to 83% in the red region of the optical spectrum.

INTRODUCTION

Earlier [1-5] authors discovered the activation effect of the interaction of solid-phase materials under action supercritical water fluid. That opens the possibility to obtain materials, which are needed and widely used in various branch of industry.

This ceramic has a good light transmission in the near ultraviolet, visible and infrared regions of the optical spectrum, exceeding even optical properties of sapphire and aluminum oxynitride. The high optical transmittance in a wide frequency range can be used in any kind of ceramic products of optical, electronic, atomic and space industry. From optical magnesia ceramics can be made transparent tube for high-intensity light source, the substrate of integrated circuits, missile radomes, window in various optical systems, as an example, for infrared laser. Great need for products of optical ceramics is limited by deficit of high-quality raw material for the production of the corresponding ceramics. Our investigations dedicated the study the possibility of using supercritical water fluid as the reaction medium for the synthesis of fine-crystalline magnesium spinel.

This appropriate technology allows obtaining a high-purity product, the raw material for optical magnesia ceramics.

MATERIALS AND METHODS

For producing of $MgAl_2O_4$ was used mechanical mixture of magnesium oxide MgO (high purity grade) and aluminum hydroxide $Al(OH)_3$ mark "MDG" (Russia) or AlOOH (boehmite) mark SB-1 UHPA (Germany). As doping agents were $AlCl_3$ and the organic agents:
$NH_4C_2H_3O_2$ and 1,2,3- propanetriol or 1,2-ethanediol.

The synthesis was carried out in laboratory autoclaves. Stoichiometric mixture of reagents was placed in a stainless steel container in autoclave of 14 - 18 cm^3. The pressure of water vapor carries out by evaporation of water, placed into the space between the walls of autoclave and containers with the starting material. The synthesized products were investigated by physical - chemical methods. X-ray analysis of the synthesized products was performed using X-ray powder diffractometer “STADI P STOE” with a CuKα.The scanning electron microscope SEM "Jeol JSM 6390 LA" was used to obtain SEM- images of produced materials. The light transmittance of the ceramic plates in UV- region of the spectrum was measured with Specord M-40 and in IR-region with Fourier-spectrometer EQUINOX 55/S.

RESULTS

As shown by the authors [1], the formation of solid complex oxides in SCWF proceeds via an intermediate step of hydrating the starting materials. In this case, to the appearance of fine-crystalline $MgAl_2O_4$ precedes formation AlOOH, Mg $(OH)_2$ and intermediate product of interaction of components, containing the magnesium and aluminum - $Mg_2Al~(OH)_7$.

The XRD pattern of the synthesis products spinel at 250°C is shown in **Figure 1a**.

Reflex of $Mg_2Al~(OH)_7$ is recording of 11° - 2Theta. In these conditions formation of spinel is not yet observed.

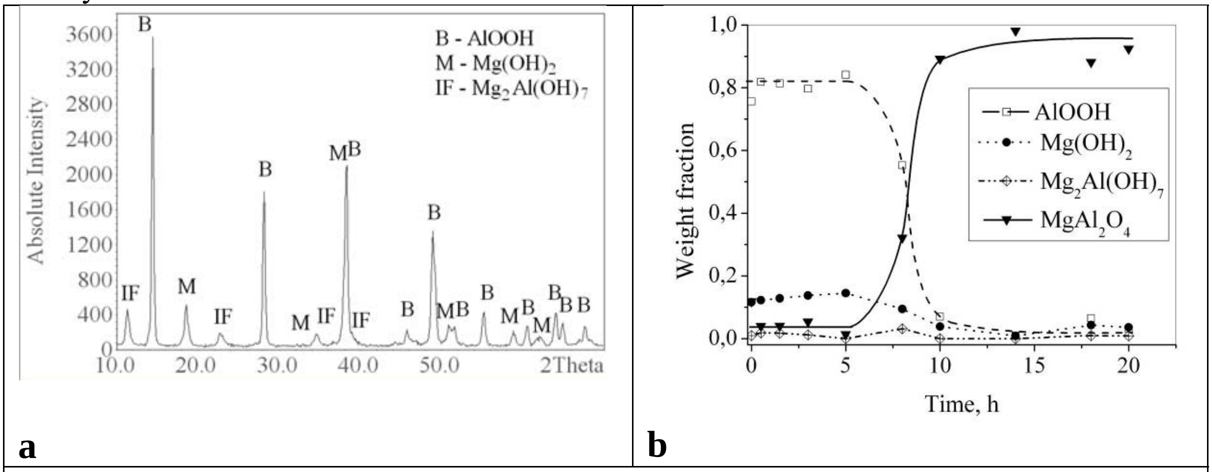


Figure 1. a) XRD pattern (Cu-K_a) of products interaction $Al(OH)_3$ and MgO with additive $AlCl_3$ (0,284 mol%) at 230°C, P=2,3 MPa during 20 h.; **b**) The change of products composition during reaction of this mixture in medium of supercritical water fluid at 400°C (P=26 MPa).

At the transition in the supercritical conditions (400°C, P = 26 MPa) the interaction of precursors intensified. Transformation kinetics of the reaction products were given in **Figure 1b.**

Complete conversion of the reaction products into spinel takes place only after heating the reaction system under SCWF during fifteen hours. At the same time, the intermediate products practically were evanesced. On the basis of the investigations results of kinetics and mechanism of precursors conversion, the stepwise spinel synthesis was selected, as the optimum: sequentially in subcritical and then in supercritical conditions.

The addition of various activators changes both time of spinel formation, as well as morphology and sizes of crystals.

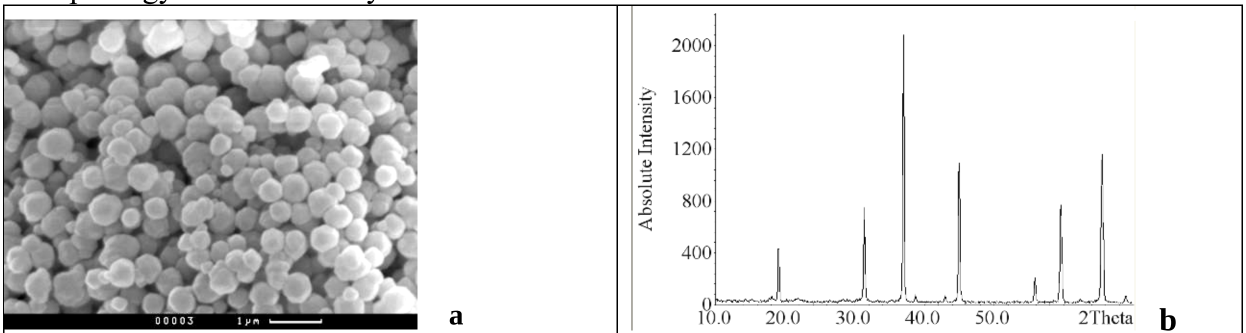


Figure 2. SEM- image (**a**) and XRD pattern (**b**) of $MgAl_2O_4$ synthesized from $Al(OH)_3$ and MgO with additives NH_4CH_3COO and $Mg(C_2H_3O_2)_2$ at 250°C and then in SCWF at 400°C (P = 26 MPa).

In **Figure 2, 3** and **4** were shown electron-microscopic photos and X-ray diffractions of spinel samples synthesized using various activators. Habitus of spinel changes from spherical (**Figure 1**) to bipyramidal (**Figure 4**) and crystals size from 0,2 to 3,0 μm.

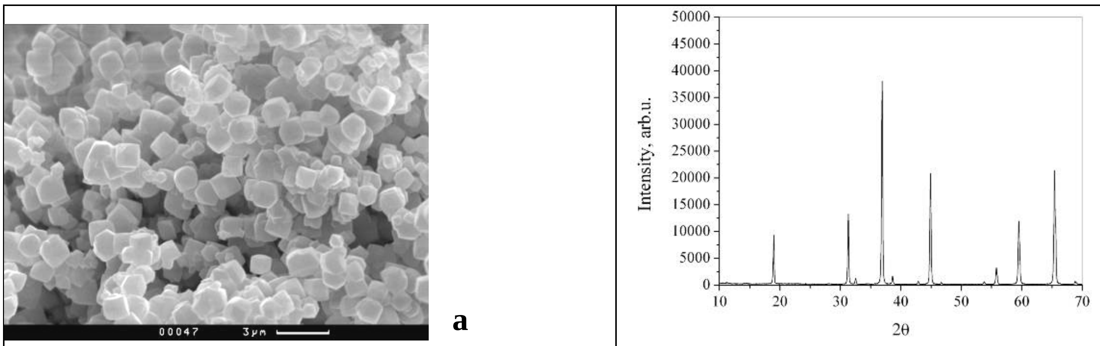


Figure 3. SEM- image (**a**) and XRD pattern (**b**) of $MgAl_2O_4$ synthesized from boehmite (ALOOH) and MgO at 250°C and then in SCWF at 400°C (P = 26 MPa) with additive 1,2-ethanediol.

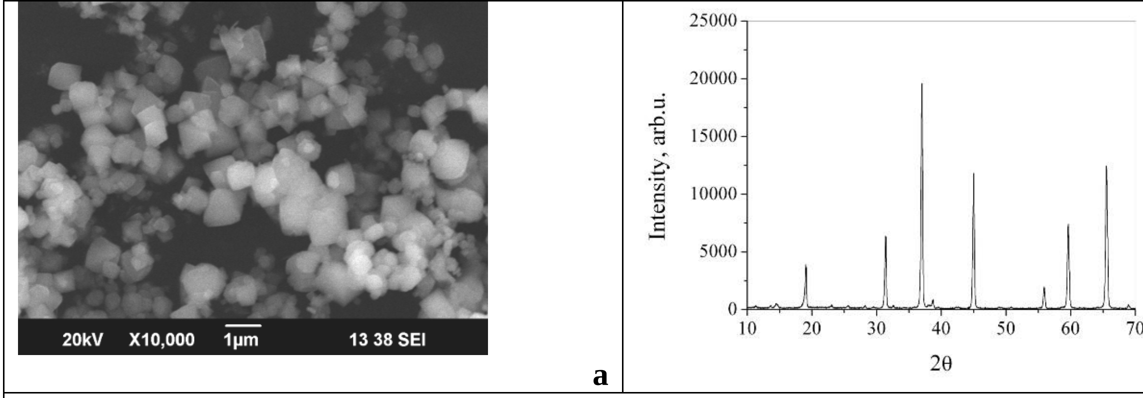


Figure 4. 3776 SEM- image (**a**) and XRD pattern (**b**) of $MgAl_2O_4$ synthesized from boehmite and MgO at 230°C and then in SCWF at 402 °C (P = 26 MPa) with additive 3,5%1,2,3- propanetriol.

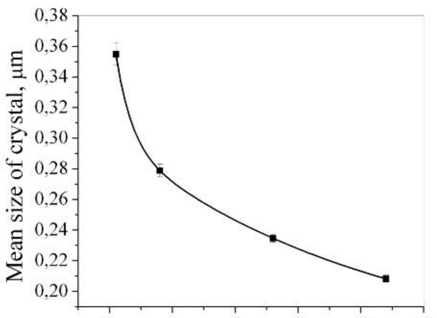


Figure 5. Dependence of the size of synthesized spinel crystals on the concentration of added activator 1,2,3-propanetriol.

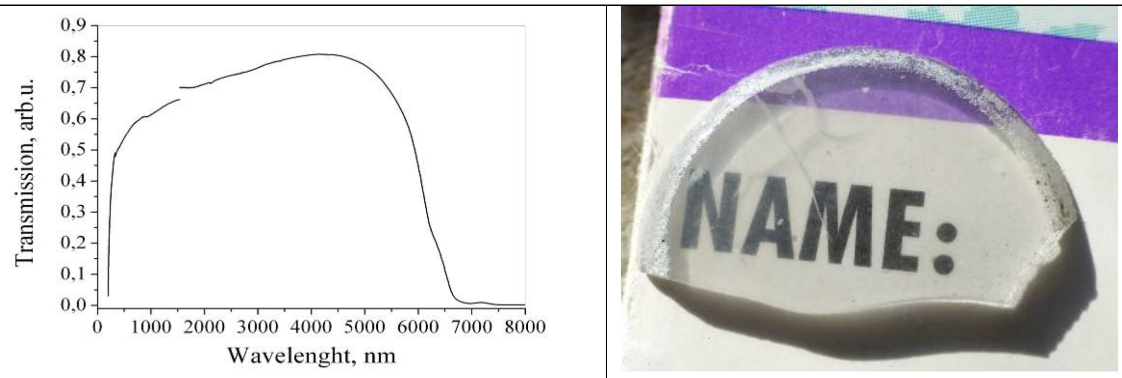
The increase of the activator concentration, for example, results in reduction of the crystals size of synthesized spinel (**Figure 5**).

The fine-crystalline magnesium spinel, synthesized in water fluid, proved oneself as perfect raw material for production transparent ceramic.

Magnesium spinel ($MgAl_2O_4$) is polycrystalline transparent ceramic with a cubic crystal structure with an excellent optical transmission from 0.2 to 6.0 micrometers [6-8]. It has been shown to possess superior optical properties within the infrared IR-region.

Polycrystalline transparent magnesium aluminate spinel ceramics was fabricated from synthesized fine-crystalline spinel by hot-pressing (HP) with following hot isostatic pressing (HIP).

This spinel ceramics possessed light transmission up to 83% (**Figure 6**).



a **b**

Figure 6. The light transmission (**a**) of the transparent magnesium spinel ceramics from fine-crystalline spinel synthesized in SCWF (**b**).

CONCLUSION

Our investigations have shown the possibility of production in supercritical water fluid the fine-crystalline spinel ($MgAl_2O_4$) with crystals size of 0.2 to 2.0 microns and the shape from spherical to octahedral. The changing of size and shape of the crystals is achieved by introducing into the reaction medium of certain organic compounds, or doping elements, and by varying parameters SCWF.

In water fluid the formation of spinel crystals from mixture of solid oxides of magnesium and aluminum goes through a stage of deep hydration of reagents. This process is realized already in subcritical water vapor. In supercritical fluid diffusion interaction of reagents with formation of spinel structure occurs. Then, in SCWF, as a result of the oriented cocrystallization nanocrystals, micron particles with well-formed faces arise.

By developed method powders of pure and doped magnesium spinel were obtained.

The main destination synthesized fine-crystalline spinel - its use as a raw material in the manufacture of transparent magnesia ceramics. Our proposed method of production of powder magnesium spinel - raw materials for the fabrication of transparent ceramics allows avoiding ecological complications and simplifies procedure of preparation start material for manufacturing ceramics, which results in reduction of industrial expenses.

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