SYNTHESIS OF FINE-DISPERSED YTTRIUM-ALUMINUM GARNET $Y_3Al_5O_{12}$ VIA SOL-GEL TECHNIQUE

V.G. Sevastyanov[1], E.P. Simonenko[1,2], N.P. Simonenko[1], N.T. Kuznetsov[1]

[1]N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninsky prosp. 31, 119991 Moscow, Russia
[2]M.V. Lomonosov Moscow State University of Fine Chemical Technology, Vernadskogo prosp. 86, 119571 Moscow, Russia
**v_sevastyanov@mail.ru*

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Abstract

Synthesis of fine dispersed mesoporous powder of yttrium-aluminum garnet $Y_3Al_5O_{12}$ (YAG) was performed using the sol-gel technology based on solution of alkoxyacetylacetonates of metals. The microstructure of the xerogel was studied by scanning electron microscopy, also the formation of mesopores was revealed. The temperature range 850 -950ºC in which crystallization of $Y_3Al_5O_{12}$ oxide from the derived xerogel takes place in the dynamic mode was determined using the combined TGA/DTA/DSC analyzer. It was established that during isothermal processing of the xerogel for 1 hour, the temperature of garnet phase formation can be lowered to 800°C. It was shown that at lower temperatures (400, 450, 500°C), even with longtime calcination (6 hours), x-ray amorphous powders are formed with a developed surface - specific surface area 230-350 m^2/g. The growth of synthesized powder particles was studied by sintering for 2 and 4 hours at temperatures 1000, 1200 and 1400°C.

Introduction

Yttrium-aluminum garnet $Y_3Al_5O_{12}$ is one of the most practically important of refractory compounds due to a number of its beneficial properties – high melting point, phase stability over a wide temperature range, the possibility for substitution of atoms on any from a number of rare earth elements without destroying the structure. The most prominent areas of application of this substance are the optics, laser technology and obtaining of luminophors (when doped, for example, with atoms of rare earth elements).

Currently $Y_3Al_5O_{12}$ is of great interest as a component of high-temperature composite materials, as well as the thermal barrier and protective coatings. Thus, due to high creep resistance of this material at elevated temperatures increases the amount of papers on obtaining of continuous fibers based on yttrium-aluminum garnet composites $Y_3Al_5O_{12}/Al_2O_3$ and eutectic $Y_3Al_5O_{12}$-Al_2O_3. Since was established that the thermal conductivity of the yttrium-aluminum garnet both at room and high temperatures is small, it is used as a component of thermal barrier/protective coatings, especially multilayer [1-3]. In addition, the ability to oxygen diffuse through $Y_3Al_5O_{12}$ is less than that of yttria-stabilized zirconia (YSZ - a well-known agent for thermal barrier coatings) for 10÷15 orders, in [3] was pointed an increase in the phase stability of YSZ in the case of a second thermal barrier layer $Y_3Al_5O_{12}$, due to the suppression of the diffusion layer of yttrium yttrium-stabilized zirconia.

One of the advantages of application of this compound as a component of high-temperature composites is the lack of interaction between silicon carbide and $Y_3Al_5O_{12}$ while heating at atmospheric and elevated pressures. It is used by Japanese researchers in the technology of obtaining of extremely dense SiC/SiC composite by NITE-process (the density of obtained SiC matrix modified with oxide additives is close to the calculated values).

Despite the fact that the development of methods of synthesis, study of properties and practical use of yttrium-aluminum garnet run for a long time, many problems are still not fully resolved. Especially it concerns the development of methods for the synthesis of nanostructured $Y_3Al_5O_{12}$.

One of the advantages of sol-gel technology for production of nanocrystalline YAG is principle possibility of the synthesis of this compound in the form of not only the powder or thin film on the surface of products, but also posibility to obtain refractory matrices directly in the volume of the composite material.

To carry out the controlled hydrolysis of metal precursors, in a solution of metal alkoxides is often introduced acetylacetone to form a more efficient precursor - alcoxy acetylacetonates of metals. From our point of view, the synthesis of hydrolytically active solutions of mixed ligand metal compounds is more efficiently to carry out by destructive substitution of the chelating ligand by thermal treatment of β-diketonate complexes in an excess of high-boiling alcohol [4-8].

The aim of the work is to obtain hydrolytically active solution of alkoxyacetylacetonates of aluminum and yttrium, synthesis on its basis of fine powder of yttrium-aluminum garnet using sol-gel techniques, as well as the study of its sintering at different temperatures.

1. An Experimental

1.1 Synthesis of precursors

In order to obtain hydrolytically active yttrium-aluminum-containing solution, acetylacetonates of corresponding metal in a given ratio (62.5 mol.% $[Al(C_5H_7O_2)_3]$ - 37.5 mol.% $[Y(C_5H_7O_2)_3]$) were subjected to heat treatment in an environment of isoamyl alcohol at a temperature of 131±3°C for four hours at reflux. The total concentration of metals was 0.2 mol/l. The process resulted to destruction of coordinated chelate ligand, the alkoxide group of the alcohol-solvent occupies the vacant coordination site, in this case, iso-$C_5H_{11}O$-fragment. With the use of spectrophotometric monitoring of the substitution process by reduction of the intensity of the absorption band of the coordinated acetylacetonate ligand (λ = 300 nm) the degree of substitution was revealed to be ~90%.

1.2 Hydrolysis and gelation

Hydrolysis of the synthesized precursor was carried out by gradual introduction of distilled water in heated to a temperature of ~70°C solution under stirring. When adding 1 vol.% water relating to the volume of hydrolytically active solution, the formation of transparent gel was observed in 20 minutes, Tyndall effect was observed. The gel was dried at 70°C in a vacuum oven until constant mass with the formation of xerogel. Scanning electron microscopy performed by three-beam workstation NVision 40, Carl Zeiss, (Fig. 1a) showed that the drying of the gel lead to porous system having pores with a diameter of ~60-90 nm and mesopores with a diameter of 30 nm, the amount of mesopores being prevalent (Fig. 1b).

Map of the distribution of the target elements - aluminum and yttrium - on the surface of the xerogel particles obtained by energy dispersive analysis shows that all parts of xerogel contain aluminum and yttrium - Fig. 2.

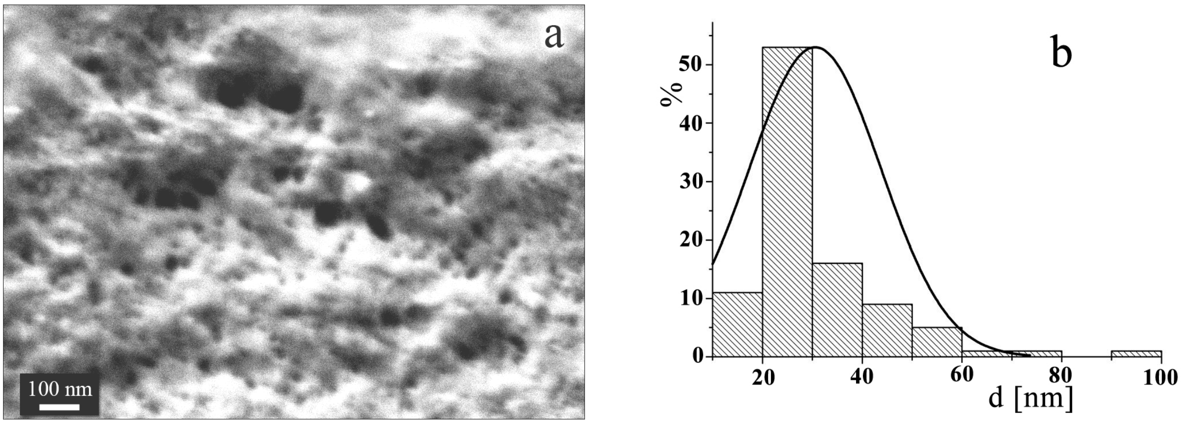


Figure 1. The microstructure of the surface of the particles of yttrium-aluminum-containing xerogel (and SEM) and the corresponding pore size distribution (b)

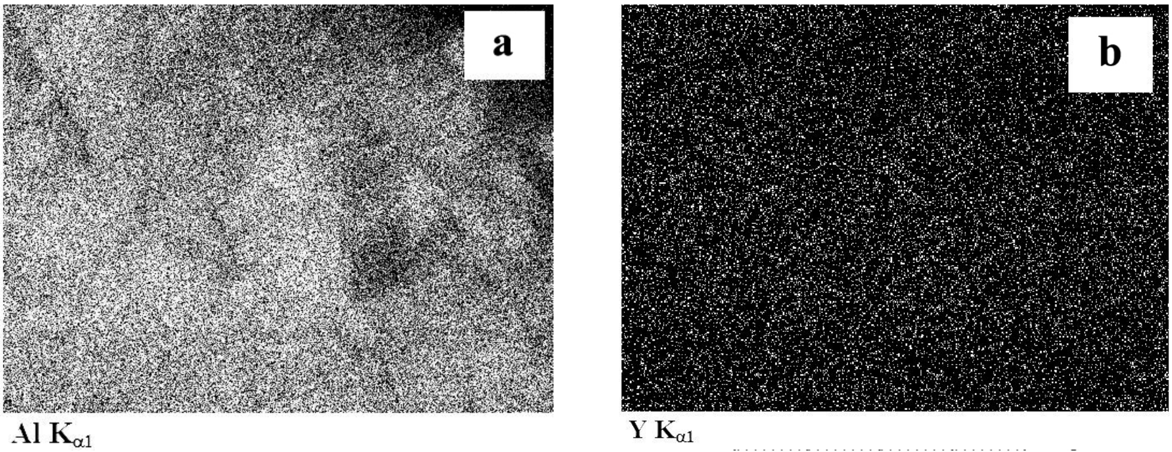
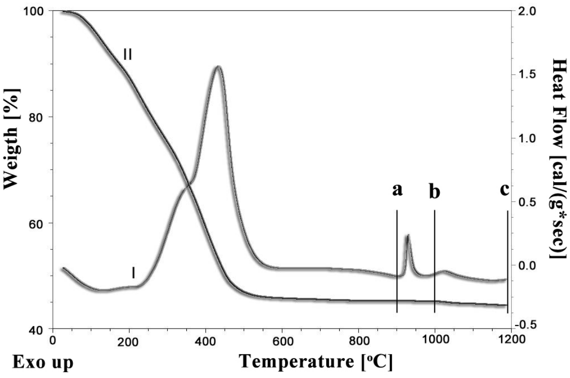


Figure 2. The distribution of the target elements - aluminum (a) and yttrium (b) at the particle surface of xerogel

1.3 Investigation of obtaining conditions of YAG phase

In order to choose the conditions of synthesis of yttrium-aluminum garnet phase at the lowest temperatures, the resulting xerogel was studied by thermal analysis in a flow of synthetic air (combined TGA/DSC/DTA analyzer SDT Q-600). The process was carried out in an alumina crucible in the temperature range 20-1200ºC with heating rate of 20º/min (flow rate - 100 ml/min, the average mass of the sample - 30-60 mg). The curves of DSC and TGA for the sample are shown in Figure 3.



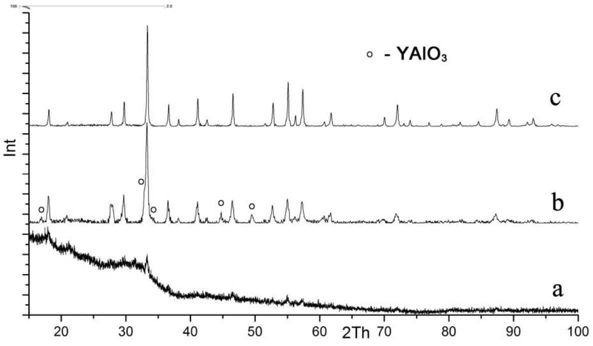


Figure 3. DSC (I) and TGA (II) curves of xerogel heated to a temperature of 1200ºC in a flow of air

Figure 4. XRD patterns of products obtained by heating of xerogel in DTA up to temperatures of 890 (a), 990 (b) and 1200ºC (c)

There are two well-resolved peaks on the DSC curve corresponding to the exothermic effects. The first peak with a shoulder is in the temperature range 220 ÷ 550°C, which probably corresponds to the desorption of gases from the surface, removal of the solvent and the oxidation of organic fragments contained in the xerogel. This confirms the TGA curve - in this interval is the main mass loss, about 55%; above the temperature of 550-600ºC the mass change is less than 1%. The second thermal effect lies in a narrow temperature range 920÷970°C, and obviously corresponds to the crystallization of the yttrium-aluminum garnet. In addition, there is a low-intensity broadened peak with a maximum of ~ 1050ºC.

In order to clarify the processes corresponding to the observed exothermic effects, the XRD analysis of the products, which were formed under dynamic conditions of heating in the thermal analysis to the temperatures of 890 (a), 990 (b) and 1200ºC (c), was carried out – corresponding XRD patterns are shown in Figure 4.

As one can see, the dynamic heating at 20 º/minute to a temperature of 890ºC resulted to formation of mainly X-ray amorphous powder, which has weak X-ray reflections corresponding to the phase of yttrium-aluminum garnet with parameter 12.00(2) Å. Heating to 990ºC, i.e. after the exothermic effect, which is observed on the thermogram in the range 920÷970°C, leads to appearing of not only main phase reflections of $Y_3Al_5O_{12}$ (approximate average size of the crystallites amounted to 40 nm), but additional reflections corresponding to the $YAlO_3$ phase - on the curve 4b they are marked by circles. However, under dynamic heating of xerogel to a temperature 1200ºC on the XRD pattern of the product there are no reflections of $YAlO_3$ phase hexagonal impurity. Calculation by Scherrer formula allowed us to determine the size of the crystallites, which was 90±2 nm.

These experiments suggest that, apparently, exothermic effects at temperatures above 920°C correspond to the processes of crystallization of $Y_3Al_5O_{12}$ and $YAlO_3$ phases.

As can be seen from Fig. 5, the microstructure of the $Y_3Al_5O_{12}$ particles, obtained by dynamic heating in the conditions of thermal analysis to a temperature of 1200°C, is significantly different from that of xerogel: there is sintering of nanosized particles of yttrium-aluminum garnet with the formation of a uniform porous particle consisting of grains with a size of 70-120 nm. The pore size is 15-25 nm and large pores are not observed - Fig. 5c.

1.4 Synthesis of $Y_3Al_5O_{12}$ during isothermal calcination of xerogel

To identify the minimum temperature of crystallization of $Y_3Al_5O_{12}$ we carried out experiments on dynamic heating with subsequent exposure at temperatures of 600, 700, 800 and 900ºC in a flow of synthetic air for 1 hour. X-ray analysis showed that under these conditions the formation of yttrium-aluminum garnet phase occurs at 800ºC (corresponding XRD patterns are shown in Figure 6), while at lower temperatures, even when exposed for 1 hour, crystallization does not occur.

In addition, it was found that the only phase formed is a phase of yttrium-aluminum garnet without the presence of $YAlO_3$ phase, the size of the crystallites was 33 nm (800ºC) and 34 nm (900ºC), which is much smaller than that for the synthesized under dynamic heating up to 1200ºC.

Laser mass spectral elemental analysis showed that the deviation from the molar ratio of metal atoms n(Al):n(Y)=5:3 is less than 1%. The main impurities are carbon and chlorine (the content of ~ 0.3 at.%); the content of other impurities is less than $1 \cdot 10^{-2}$ at.%.

Thus, it is shown that the isothermal exposure for 1 hour can reduce the temperature of the synthesis of crystalline $Y_3Al_5O_{12}$ more than at 150ºC in comparison with the value obtained in the dynamic mode.

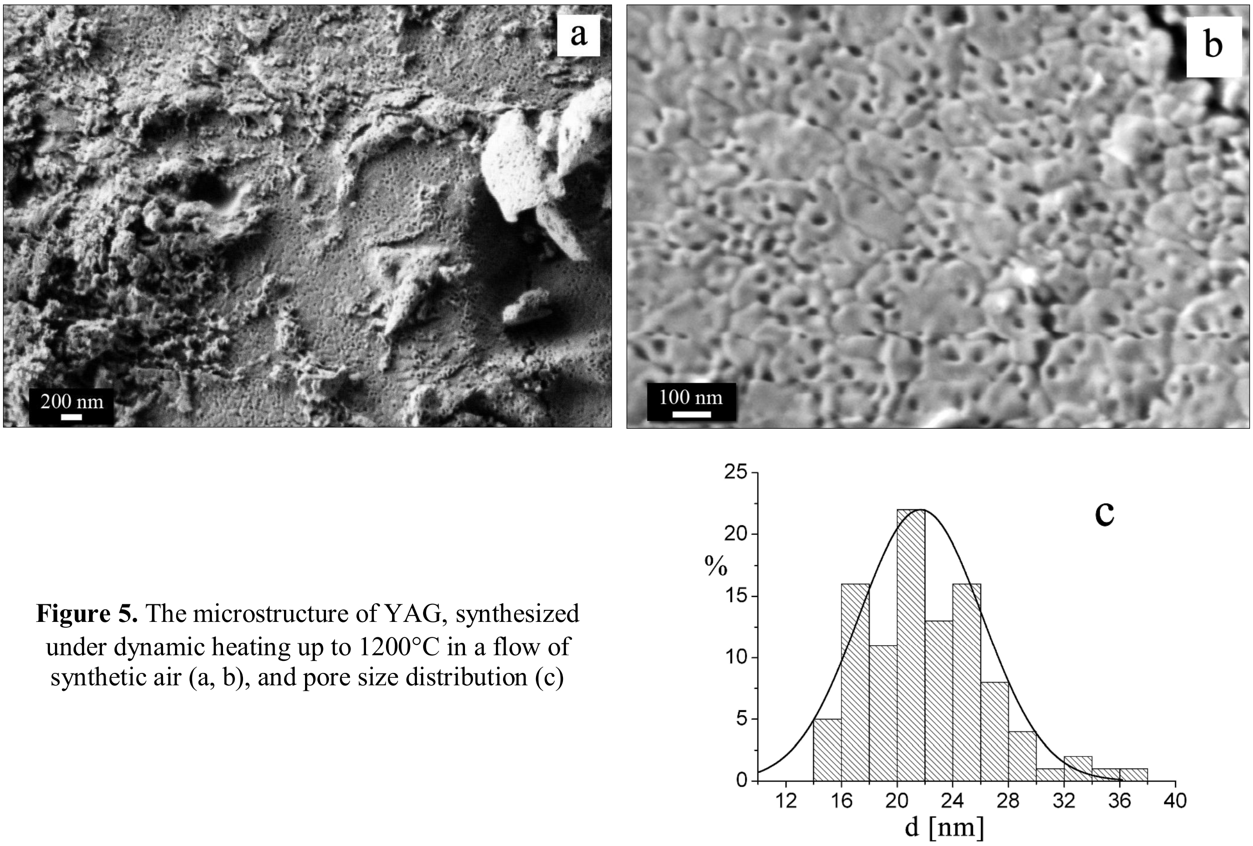


Figure 5. The microstructure of YAG, synthesized under dynamic heating up to 1200°C in a flow of synthetic air (a, b), and pore size distribution (c)

Additional studies on xerogels calcination at temperatures 400, 450 and 500ºC for 6 hours to burn out the excess carbon showed that under these conditions there is no formation of crystalline products. The resulting X-ray amorphous products have developed specific surface area, which is confirmed by measurements by the BET (adsorption weight device, N_2, 77 K). The values obtained are shown in Table 1. As can be seen, for X-ray amorphous powders they are 235÷350 m^2/g, while for the calcined at 800ºC for 1 h partially amorphous product - 124±2 m^2/g.

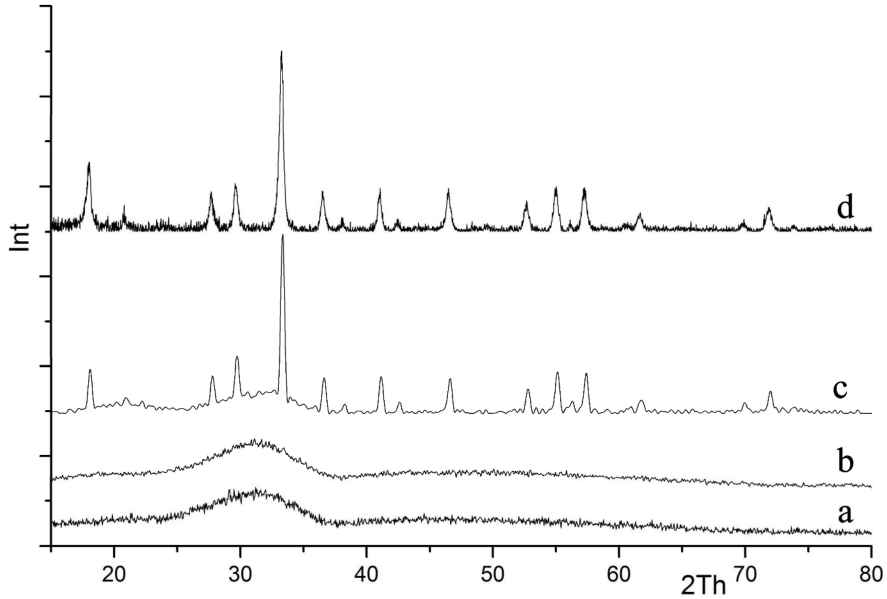


Figure 6. XRD pattern of powders obtained by dynamic heating of xerogel in air flow and exposed at a given temperature for 1 h at: (a) - 600, (b) - 700, (c) - 800 (d) - 900ºC

Table 1. The values of specific surface area S of $Y_3Al_5O_{12}$ oxide powder, obtained at different temperatures

Synthesis temperature, ºC	**Time of heat treatment, h**	**S, m^2/g**
400	6	350±5
450	6	300±5
500	6	235±5
800	1	124±2

1.5 Investigation of particles coarsening during sintering of the synthesized powder

To study the processes of coarsening of powder particles of $Y_3Al_5O_{12}$, synthesized after calcination of xerogel at 500ºC for 6 hours, the sintering of powders was carried out at temperatures 1000, 1200 and 1400ºC for 2 and 4 hours. X-ray analysis showed the formation of single-phase products - YAG without admixtures of other phases. Crystallites calculated by Scherrer equation are shown in Table 2.

The data collected in Table 2 shows that even at sintering at 1000ºC for 2 hours there is a significant decrease in specific surface area values up to 5-9 m^2/g, which practically does not change with longer heat treatment, as well as using higher temperatures - 1200 and 1400ºC. This may indicate that the porosity and morphology of the powders, which were formed under the most mild conditions of sintering (1000ºC, 2 h), do not undergo significant changes with an increase in temperature and time of thermal treatment.

Table 2. The values of crystallites size, calculated by the Scherrer formula, L (nm) for the powders subjected to heat treatment at different temperatures and exposure time

The time of sintering, h	**The temperature of heat treatment, ºC**					
	1000		**1200**		**1400**	
	L, nm	**S, m^2/g**	**L, nm**	**S, m^2/g**	**L, nm**	**S, m^2/g**
2	80±10	7±2	140±15	7±2	230±15	8±2
4	90±10	5±1	180±15	7±3	230±15	6±2

At the same time the influence of sintering temperature on the size of the crystallites is clearly seen - there is almost a linear increase with increase of temperature of heat treatment. With increasing exposure time the crystallite size increases slightly.

Conclusion

With the use of synthesized hydrolytically active alkoxoacetylacetonates solutions of aluminum and yttrium, yttrium-aluminum-containing gel was produced by sol-gel method, and formed xerogel after drying. Scanning electron microscopy showed the formation of porous system having pores with a diameter of preferably less than 30 nm (i.e., mesopores), although a small amount of pores with a size of 60-80 nm.

Thermal analysis of the behavior of xerogel in air showed that the DTA curve has several peaks corresponding to the exothermic process. Thus, in the temperature range 220÷550°C, taking into account the data on mass loss (about 55%), occurs oxidation of organic xerogel fragments, together with the desorption of gases from the surface and removal of residual solvent. At temperatures above 550ºC the mass loss is practically not observed.

In the temperature range of 920-970ºC there is a narrow peak which is probably associated with the processes of crystallization of complex oxides of aluminum-yttrium. XRD analysis of the products of xerogel heated in air to a temperature of 990ºC shows that although the main phase is yttrium-aluminum garnet, but there is an impurity of $YAlO_3$ phase. The product of heating of xerogel to a temperature 890ºC is X-ray amorphous, despite weak reflections of $Y_3Al_5O_{12}$ phase on the backdrop of the halo corresponding to amorphous sample. In the XRD pattern of the product, heated in an air flow to a temperature of 1200ºC, there are only reflections of yttrium-aluminum garnet phase.

Low-intensity peak with a maximum at ~1050ºC can be attributed to burnout of residual carbon, encapsulated in the bulk oxide, as while crystallization there is a change in structure of the material, the disclosure of previously closed porosity.

Exposure of xerogels in air at temperatures 600, 700, 800 and 900ºC for 1 h, which was carried out in order to lower the temperature of crystallization of yttrium-aluminum garnet, allowed to draw a conclusion about the possibility of synthesis of nanocrystalline $Y_3Al_5O_{12}$ at a temperature of 800ºC, while at 700ºC the crystalline products were not formed. The size of the crystallites calculated by the Scherrer formula amounted to 30-35 nm, which is significantly lower than for the product of dynamic heating in air flow during the thermal analysis to a temperature of 1200ºC (~ 90 nm).

Additional studies of the products of long-term (6 hours) calcinations of xerogels in air at temperatures 400, 450 and 500ºC were conducted. All formed oxide products were X-ray amorphous and had a high specific surface area - 230-350 m^2/g

Oxide product obtained at 500ºC was used for the study of coarsening processes during sintering of the particles under different conditions - at temperatures 1000, 1200 and 1400ºC for 2 and 4 hours. The measured specific surface area for the products obtained in all these processes, practically has not changed - 5-9 m^2/g However, the size of crystallites calculated by the Scherrer formula, significantly (almost linearly) increased with increasing the heat treatment temperature. Effect of sintering time has less effect, especially at the maximum temperature.

Thus, using the sol-gel technique based on the synthesized hydrolytically active solutions of alcoxyacetylacetonates of aluminum and yttrium, yttrium-aluminum garnet nanocrystalline powders were obtained at moderate temperatures (800-900ºC), as well as X-ray amorphous oxide powders of the given composition having a high specific surface area of 230 - 350 m^2/g, which are promising not only as a starting powders for the synthesis of oxide ceramics in relatively mild conditions, but also as ingredients for functional materials, such as chemical gas sensor systems.

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