

Transparent ceramics of yttrium-aluminum garnet ($Y_3Al_5O_{12}$) from nanocrystalline powders obtained by co-precipitation

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Nanosized powders of yttrium-aluminum garnet $Y_3Al_5O_{12}$, (YAG) have been obtained by chemical co-precipitation. The effect of the powder structure and morphology on the compactibility and sinterability has been studied. The optimal combination of these properties has been found in the YAG powder having the average grain size of 80 nm synthesized at 1200°C. Using the vacuum sintering at 1750°C, the transparent $Y_3Al_5O_{12}$ ceramics has been obtained having the density 99.9 % of theoretical value and the transmission coefficient 60 % in the wavelength range of 400 to 800 nm.

Методом химического соосаждения получены наноразмерные порошки иттрий-алюминиевого граната $Y_3Al_5O_{12}$ (ИАГ). Изучено влияние структуры и морфологии порошков на их прессуемость и спекаемость. Установлено, что оптимальным сочетанием этих характеристик обладает порошок ИАГ со средним размером зерна 80 нм, синтезированный при температуре 1200°C. Методом вакуумного спекания при 1750°C получена прозрачная керамика $Y_3Al_5O_{12}$ с плотностью 99,9 % от теоретической и коэффициентом пропускания 60 % в области длин волн 400–800 нм.

The development of transparent ceramics based on refractory oxides, in particular, yttrium-aluminum garnet $Y_3Al_5O_{12}$, suitable for use as active laser matrices, is to be noted among the most important recent advances in the field of novel materials for photonics [1–3]. The yttrium-aluminum garnet ceramics for lasers is essentially equivalent to single crystals in the transparency, optical losses and the spectral generation characteristics [4]. The advantages of the optical ceramics consist in enhanced physico-mechanical properties, the possibility to the activator introduction within a wider concentration range and its homogeneous distribution. The ceramic technologies are less expensive and impose less restrictions on the article shape and size.

A general principles in the optical ceramics manufacturing are the use of weakly agglomerated nanosized high-purity powders as the initial materials as well as the high-temperature sintering technique. The use of finely dispersed powders having a developed free surface provides a considerable activation of the solid phase interaction, because the surface and grain-boundary diffusion processes predominate in such materials over the volume ones. The nanosized powders are manufactured usually by relatively inexpensive "wet chemistry" methods that do not require any sophisticated equipment, in particular, by chemical co-precipitation [5, 6], sol-gel [7] or hydrothermal [8] techniques. The chemical co-precipitation, under certain realization conditions, is believed to be the most

simple, inexpensive, and prospective technique to obtain fine powders of oxides and compounds thereof providing the development of ceramics with the pre-specified structure and properties. Varying the synthesis conditions by using of various initial salts and precipitants, pH, temperature and mixing intensity of the reaction mixture, the precipitate aging temperature and duration and its thermal treatment conditions intended to obtain the YAG phase, it is possible to obtain nanosized powders of various phase compositions, particle sizes, dispersity, and agglomeration degree. Since the nanosized particles form rigid three-dimensional agglomerates, it is rather difficult to compact them to obtain a dense workpiece suitable for the vacuum sintering. The inter-agglomerate pores being formed during the consolidation of such powders result in the residual porosity in the sintered ceramics and thus hinders the manufacturing of transparent ceramics that should have a density close to the theoretical one.

The purpose of this work was to obtain weakly agglomerated nanosized YAG powders consisting of spherical particles suitable for compacting, to reveal the regularities of the powder morphology effect on the compactibility and sinterability, and to obtain the YAG transparent ceramics.

The nanosized garnet powders were prepared by co-precipitation from 0.5 M solutions of yttrium and aluminum nitrates ($Y(NO_3)_3$ and $Al(NO_3)_3$, respectively, both of special purity grade), using aqueous ammonia hydrocarbonate (NH_4HCO_3 , chemical purity grade). The "reverse" precipitation technique was used, i.e., the nitrate solution was added dropwise to the ammonia hydrocarbonate one, since that precipitation scheme is preferable for multi-cationic compounds, because it provides an enhanced chemical homogeneity of the precipitate, that is the garnet precursor. The precursor was heat treated at 800–1300°C for 2 h.

The differential thermal (DTA) and thermogravimetric (TG) analyses were carried out using a MOM Q-1500 derivatograph in air within temperature interval of 20 to 1000°C at the heating rate of 10 deg/min. To the X-ray phase analysis (XPA) in $Cu K\alpha$ emission, a Siemens D-500 diffractometer was used. The phases were identified using the PDF-4 card-file [9] and the EVA retrieval system included in the diffractometer software. The dilatometric measurements were done using a Netzsch 402 ED differential dilatometer in air within tem-

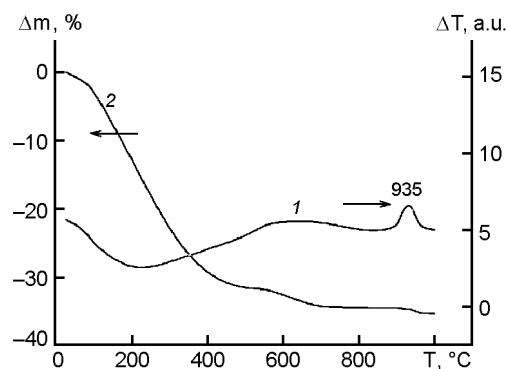


Fig. 1. Results of DTA (1) and TG (2) of YAG precursor obtained by co-precipitation of yttrium and aluminum nitrates with ammonia hydrocarbonate and dried at 120°C.

perature interval of 20 to 1500°C at the heating rate of 10 deg/min. The surface area of the powders was measured by the BET method. The average particle diameter was calculated from the relationship $d = K/S \cdot \rho$, where K is the particle shape factor equal to 6 for the spherical and cubic particles; S , the specific surface area, m^2/g ; ρ , the $Y_3Al_5O_{12}$ theoretical density equal to $4.55 g/cm^3$. The powder morphology was studied using a transmission electron microscope TEM-125 at 100 V accelerating voltage. Prior to the microscopic examination, the powders were subjected to ultrasonic treatment using a UZDN emitter at 22 kHz frequency for 45 s. Isopropanol was used as the working medium.

The YAG powders were compacted into tablets of 10 mm in diameter and 2 mm height in a metal mould for uniaxial pressing within the pressure range of 30 to 520 MPa as well as using cold isostatic pressing under 400 MPa pressure. The sample density was determined by geometric procedure. The tablets were sintered in an induction furnace at 1500 to 1750°C for 10–20 h in vacuum (the max residual pressure being 10^{-3} Pa). The ceramic microstructure was examined in reflected beams using a JSM-6390LV scanning electron microscope (SEM). To reveal the grain boundaries, the samples were polished with diamond paste followed by etching with orthophosphoric acid. The ceramics mechanical properties (microhardness and failure viscosity) were determined by micro-indentation using a PMT-3 instrument according to the standard procedure. The measurement error was 2 %.

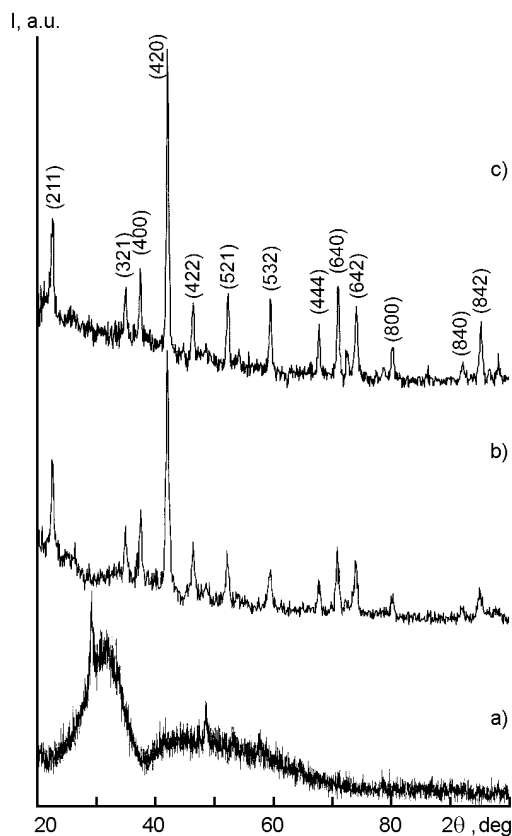


Fig. 2. X-ray diffraction patterns of the YAG precursor and powder calcined for 2 h at temperature (°C): 800 (a), 1000 (b) and 1200 (c).

To determine the formation temperature of single-phase YAG, the precursor dried at 120°C as well as its calcination products at 800–1300°C were analyzed by DTA, TG and XPA. In the TG curve (Fig. 1), a considerable mass loss (up to 27 %) was observed at temperature up to 500°C due to removal of molecular and structurally bound water and ammonia carbonate residues. The insignificant mass losses (7 and 2 %) observed in the temperature intervals of 500–700°C and 900–950°C, respectively, are due to further

decomposition of yttrium and aluminum complex carbonates being in agreement with [11]. The exotherm in the DTA curve at 938°C corresponds to formation onset of the $Y_3Al_5O_{12}$ phase.

Fig. 2 presents the diffraction patterns for YAG powders obtained by the precursor heat treatment at 800, 1000, and 1200°C. The YAG powders calcined at a temperature lower than 800°C are amorphous. The weak diffraction peaks in the diffraction pattern for the powder calcined at 800°C (Fig. 2b) evidences the crystallization onset of the amorphous phase. The diffraction pattern of the powder calcined at 1000°C (Fig. 2c) reveals a set of reflections that corresponds to the cubic $Y_3Al_5O_{12}$ modification. As the calcination temperature rises, the diffraction peaks become more and more intense and narrow, thus evidencing the particle size increase.

The morphologic study of the precursor and YAG powders (Fig. 3) shows that the particles obtained are essentially spherical and strongly agglomerated. The precursor particles of about 10 to 15 nm size form agglomerates (spherical, too) of up to 100 nm size which, in turn, form the coral-shaped conglomerates attaining several micrometers in size (Fig. 3a). The agglomeration of precursor having a complex composition $NH_4AlY_{0.6}(CO_3)_{1.9}(OH)_2 \cdot 0.8H_2O$ [5] seems to result from the formation of hydrogen bonds between the hydrate water molecules as well as from considerable capillary forces arising during the drying. The precursor agglomeration causes the agglomerated state of its processing products, too. The rigid, hardly crushable agglomerates hinder considerably the garnet powder compacting.

To synthesize the garnet phase and reduce the agglomeration, the precursor was heat treated within 1000 to 1300°C range.

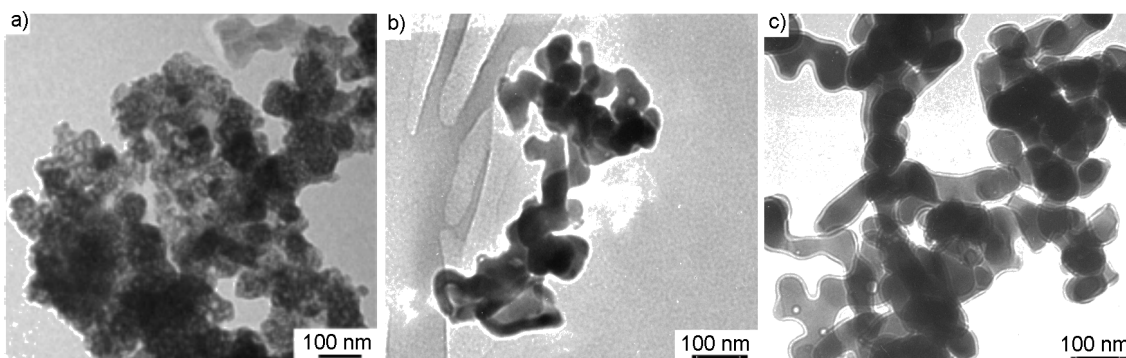


Fig. 3. Morphology of YAG powder synthesized at temperature (°C): 120 (a), 1100 (b) and 1300 (c) (TEM).

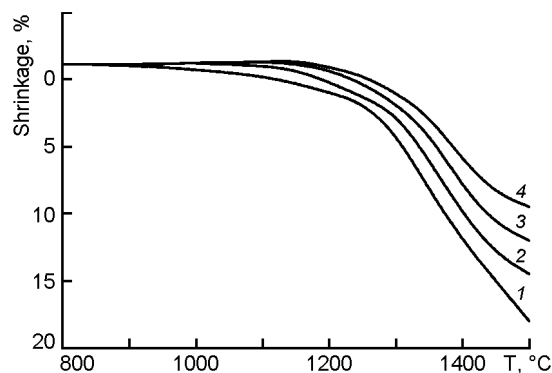


Fig. 4. Shrinkage curves of pressings made of YAG powder synthesized at temperature (°C): 1000 (1), 1100 (2), 1200 (3) and 1300 (4).

As it follows from the dilatometric data for YAG (Fig. 4a), the initial compacting stage occurs at those temperatures, i.e., the mass transfer processes are activated directed to reduction of the system surface energy. As a result of the surface diffusion of atoms that predominates at the initial mass transfer stage, the surface energy of the particles becomes reduced due to enlargement thereof. The surface state and particle size after the heat treatment was estimated from the surface area. As the calcination temperature was increased from 1000 to 1300°C, the particle surface area was reduced from 38 to 9 m²/g, while the average size increasing from 38 to 144 nm (Table). As the particle size was increased, the agglomeration extent became reduced (see Fig. 3b), because the surface interaction drops sharply as the particles become enlarged. However, at the heat treatment temperature exceeding 1200°C, the particles become aggregated with formation of contact necks (Fig. 3c). The appreciable compaction of samples observed at a further temperature elevation (see Fig. 4a) evidences an increase

Table. Specific surface area and average particle size of YAG powder

Sample No.	Synthesis temp., °C	Specific surface area, m ² /g	d_{av} , nm
1	120	71	18
2	500	64	20
3	800	44	30
4	1000	34	38
5	1100	25	50
6	1200	16	78
7	1300	9	144

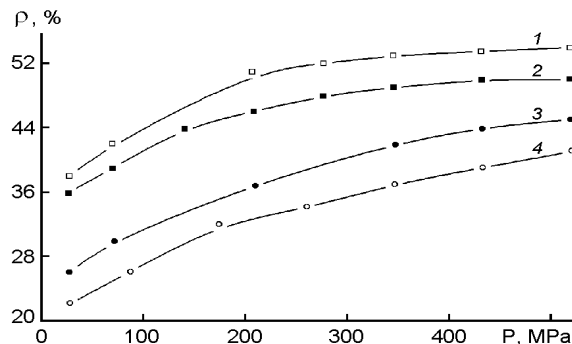


Fig. 5. Dependences of YAG pressings relative density on the compaction pressure. YAG powders were synthesized at temperature (°C): 1300 (1), 1200 (2), 1100 (3), 1000 (4).

in the contact neck area accompanied by rapprochement of the particle centers, thus, the cake requires an additional grinding prior to compacting.

To determine the powder morphology most suitable for manufacturing of high density optical ceramics, the compactibility and sinterability of the powder were studied. Those properties depend mainly on the powder agglomeration extent and surface area. Fig. 5 presents the plotted dependences of the pressings relative density on the compacting pressure (dry uniaxial compaction) for YAG powders calcined at various temperatures. The compacted sample density of the powders calcined at 1000 and 1100°C (particle size 38 and 50 nm, respectively) was low and did not exceed 44 % in the whole pressure range. After heat treatment at 1200–1300°C (the particle size being increased to 78–144 nm, Table), the powder compactibility was increased to 50–54 %, thus confirming the above conclusions on the agglomeration reduction at the particle enlargement.

To study the YAG powder sinterability, the powders synthesized at various temperatures were examined by dilatometry (Fig. 4). As the initial heat treatment temperature increases, the sintering onset temperature is shifted towards higher values, while the shrinkage at sintering is reduced. The YAG powder calcined at 1000°C shows the highest activity, however, its intense sintering results often in the zone isolation effect [12] due to inhomogeneous sample densification and, in some cases, in cracking. In turn, the powder treated at 1300°C is sintered poorly, because the surface and grain boundary diffusion mechanisms are not predominant therein due to reduced free

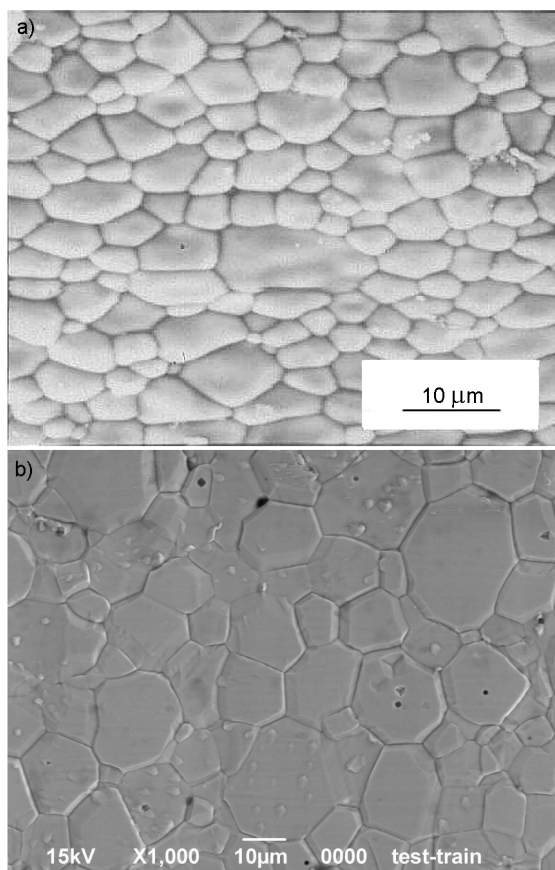


Fig. 6. Microphotos (SEM) of YAG ceramics structure after vacuum sintering at 1700°C for 10 h (a) and at 1750°C for 20 h (b).

surface. The volume diffusion mechanism of sintering becomes predominant; the volume diffusion rate is several orders lower than the surface and grain boundary ones, so the ceramic grain growth overcomes its densifying. Basing on the YAG powder compactibility and dilatometric data, the optimum sintering is provided by the garnet powder synthesized at 1200°C with the average particle size of 78 nm.

The uniaxial compaction causes non-uniform material density distribution over the pressing volume and internal stresses, that is the most clearly pronounced at increasing compaction pressure. That is why tablets first were uniaxially compacted under 30 MPa pressure and then post-compacted isostatically at 400 MPa to provide homogeneous YAG compacts for the further vacuum sintering. The compacts had a density attaining 50–52 % of theoretical one.

The compacts were sintered in vacuum at 1700–1750°C for 10–20 h. The increasing sintering temperature and duration results in the ceramic grain size enlargement from



Fig. 7. 1 mm thick $Y_3Al_5O_{12}$ ceramics sintered in vacuum at 1750°C for 20 h.

10–20 to 10–20 μm and reduced amount of residual pores (Fig. 6). The presence of closed pores not only at the grain boundaries but also inside the grains (Fig. 6b) is associated likely with a high heating rate of the sample being sintered and, as a consequence, with a fast growth of ceramic grain resulting in the pore capture. The sintering at 1750°C for 20 h results in formation of transparent YAG ceramics with the relative density of 99.9 % of theoretical one (Fig. 7) and the transmission factor of 60 % in the 400–800 nm wavelength range. The ceramics microhardness value is $H_u = 13.8$ GPa, the failure viscosity $K_c = 4.5$ $\text{MPa}\cdot\text{m}^{1/2}$, thus exceeding the corresponding values for similar crystals.

Thus, single-phase nanosized powders of yttrium-aluminum garnet $Y_3Al_5O_{12}$ have been synthesized by chemical co-precipitation followed by the precipitate heat treatment. The compactibility of the finely dispersed powders has been shown to depend on the morphology and agglomeration extent, and the sinterability, on the surface area value that defines the diffusion process character and mechanism. It has been found that when heat treatment temperature of the YAG precursor is increased from 1000 to 1300°C, the powder surface area is reduced from 34 to 9 m^2/g , and the average particle size increases from 38 to 144 nm due to activation of the surface and grain boundary diffusion, thus resulting in the reduced agglomeration extent. The optimum combination of compactibility and sinterability has been found at the $Y_3Al_5O_{12}$ powder with the average grain size of 78 nm synthesized at 1200°C. The compacts made of that powder with the relative density about 50–52 % can be prepared by isostatic compaction under pressures up to 400 MPa. Using the vacuum sintering at 1750°C, transparent YAG ceramics has been ob-

tained having the relative density of 99.9 % of theoretical one and the transmission factor of 60 % in the visible spectral range.

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Прозора кераміка ітрій-алюмінієвого гранату $\text{Y}_3\text{Al}_5\text{O}_{12}$ з нанокристалічних порошоків, одержаних методом співосадження

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Методом хімічного співосадження синтезовано нанорозмірні порошки ітрій-алюмінієвого гранату $\text{Y}_3\text{Al}_5\text{O}_{12}$ (ІАГ). Вивчено вплив структури та морфології порошоків на їх пресуємість та спіклівість. Встановлено, що оптимальні сполучення цих характеристик має порошок ІАГ із середнім розміром зерна 80 нм, синтезований при температурі 1200°C. Методом вакуумного спікання при 1750°C одержано прозору кераміку $\text{Y}_3\text{Al}_5\text{O}_{12}$ із щільністю 99,9 % від теоретичної та коефіцієнтом пропускання 60 % в області довжин хвиль 400–800 нм.