

Laser ceramic. 1. Production methods

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This section of this review discusses the main features of methods for producing a new laser material—a ceramic for the development of powerful next-generation solid-state lasers. A laser ceramic with a perfect crystalline structure and containing no impurities is virtually identical to microcrystals of the same composition in its spectral and laser characteristics. The main methods of synthesizing precursors for a laser ceramic and examples of the technological implementation of these methods are considered. © 2010 Optical Society of America.

I. INTRODUCTION

Laser ceramic is a new material of solid-state quantum electronics that was put into practice in the mid 1990s. Laser ceramic, as an active medium of solid-state lasers, possesses complex properties that ensure that it is highly competitive with both laser glasses and laser crystals, especially when solving problems of the creation of high-aperture laser elements that operate in the continuous or repeated-pulse regime.

This paper is the first of a series of articles devoted to methods of producing a laser ceramic and the properties and prospects of using it. From the materials-science viewpoint, a laser ceramic is a variety of special ceramic whose optical properties satisfy the requirements imposed on laser materials.

A polycrystalline ceramic consists of tiny, randomly oriented crystals ranging in size from hundreds of nanometers to several tens of micrometers. It is considered that polycrystalline transparent ceramic was first obtained at the beginning of the 1960s, although it is known that even ancient Chinese porcelain was fairly transparent in thin layers. The first material that had technical significance was transparent aluminum oxide.¹ Since that time, samples of transparent ceramic have been obtained from the most varied materials—oxides, fluorides, and nitrides. Along with experience in producing more and more transparent and homogeneous samples, it became understood that dense, high-purity polycrystalline material made from an isotropic substance does not differ in its optical properties from a single crystal. The light-scattering centers in a ceramic are grain boundaries, residual pores inside the grains and on their boundaries, and impurity phases, including those on the grain boundary, birefringent structures, etc. The key decision that

brought success was the concept that, to obtain a transparent ceramic, it is necessary to reduce its porosity. The presence of pores in a ceramic produces strong light scattering, even if the pores are small. For instance, to obtain transparent aluminum oxide ceramic, the concentration of pores less than 100 nm across must be lower than 0.01 vol%.² To obtain a laser-quality ceramic, the overall light scattering must be reduced to the minimum (less than 1%/cm), since the efficiency of the gain strongly falls off even for the minimum scattering.³

The first laser polycrystalline material (calcium fluoride) was probably obtained in 1966 by hot vacuum pressing of powder.⁴ The transmittance, refractive index, and optical homogeneity of the ceramic samples were close to those for a single crystal. The laser characteristics of these two materials were also similar.

It was then reported that an ordinary synthesis method had been used to obtain a transparent ceramic possessing laser properties, based on neodymium-doped yttrium oxide.⁵ Zirconium, hafnium, and thorium oxides⁶ were used as additives that make it easier to sinter the material. The lasing threshold and the slope of the efficiency in the ceramic were about the same as in commercial laser glass of that time.⁷ Nevertheless, it was not possible in the first papers to obtain a ceramic of high optical quality, comparable with the quality of single crystals and glasses.

A ceramic based on YAG with density virtually equal to the theoretical value was obtained in 1984.⁸ With and Van Dijk used SiO₂ and MgO as additives to improve the sinterability and to suppress grain growth. The starting powders were obtained by aerosol spraying of a solution of a mix of metal sulfates, followed by heating. Since that time, SiO₂ has become widespread as an inhibiting additive when sintering ceramic of the composition of YAG.

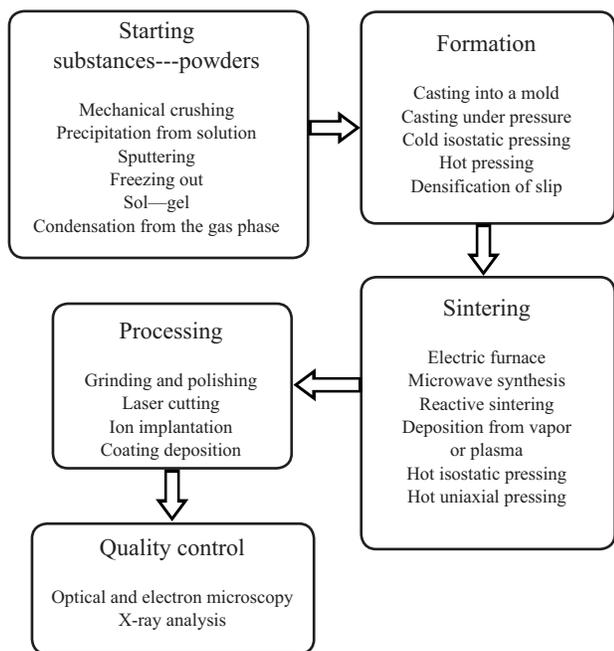


FIG. 1. Diagram of the technological process for producing a special ceramic.

The main drawback of the early ceramic samples was the high level of nonselective absorption, which ranges from 0.25 to 3 cm⁻¹.⁹ In this parameter, the ceramic was inferior to commercial single crystals and glasses by more than an order of magnitude. A breakthrough in the laser-ceramic area occurred in 1995, when a laser-quality ceramic based on YAG doped with 1.1% neodymium was demonstrated.¹⁰ The ceramic was obtained by solid-phase sintering with a grain size of about 50 μm and a relative density of 99.8%. An output power of about 70 W in the continuous regime was achieved with an efficiency slope of 28%.

Vacuum sintering of nanopowders was later used to fabricate ceramic, and ceramic samples were obtained with transparency equivalent to that of a single crystal.¹¹

The goal of this part of this paper is to analytically review the main methods of synthesizing laser ceramic. The development of powerful and superpowerful laser systems requires deep understanding not only of the spectroscopic features of ceramic by comparison with crystals and glasses, but also the material-science aspects associated with the synthesis of ceramic. The quality of the optical ceramic largely depends on the phase and granulometric composition of the starting materials. Therefore, significant attention in the review is paid to methods of synthesizing precursors and their subsequent processing.

II. METHODS OF OBTAINING A LASER CERAMIC

A. Specifics of an optical ceramic

In the most general form, the technological process of fabricating any ceramic item consists of the sequence of stages shown in Fig. 1. The first specific feature of a laser ceramic consists of the necessity of obtaining a pore-free sample with density equal in the final analysis to that of a

single crystal of the same composition. To do this, it is necessary at each stage of the process to maximize the packing density of the particles and the diffusion mobility of the atoms during sintering and to use the maximum interior compressive pressure, which is the driving force for pore removal when the ceramic is being sintered. The most widely used method of densifying the starting materials and the sintered ceramic is the supplementary use of external pressure—uniaxial, isostatic or magnetic-pulse. Of these three methods, isostatic pressing is the most complex and expensive, but at the same time the most effective process. Below we give examples of the fact that, with a reasonable method of preparing the mix when preparing a laser ceramic, it is possible to avoid the stage of hot or cold isostatic pressing.

A second specific feature of optical ceramic is that the boundaries between the grains must be optically perfect—they must contain no foreign impurities and must have the narrowest possible disordered region.

B. Requirements on the starting materials for synthesizing a laser ceramic

In synthesizing a transparent ceramic, the composition and quality of the starting materials are among the critical factors that determine the quality of the resulting product. Below we enumerate the main factors that affect the quality of an optical ceramic.

1. Particle size

The driving force and the sintering time for producing a sample of dense ceramic are determined by the surface curvature of the particles. According to Herring's rule, if powders of identical shape but different size are sintered under identical experimental conditions, the times needed to obtain samples of identical density relate to each other as

$$\frac{t_2}{t_1} = (\lambda)^\alpha, \quad (1)$$

where λ is the ratio of radii of the particles, and α is an exponent which—for example, for the case in which the diffusion rate of atoms in the lattice is the limiting stage of the sintering process—equals 3.¹² The use of nanopowders makes it possible, on one hand, to improve the sinterability of the ceramic and, on the other, to optimize the conditions for collapse of the pores.¹³

Very small particles (less than 10 nm) are hard to work with, in particular for pressing. The preferable particle size for fabricating a transparent ceramic therefore ranges from 10 to 100 nm.

2. Particle distribution over sizes

It must be as narrow as possible, in order to avoid different shrinkage around different particles when they are sintered. On the other hand, monodisperse particles form looser packing than powders fabricated from particles of different but controlled sizes, in order to fill the intermediate space.

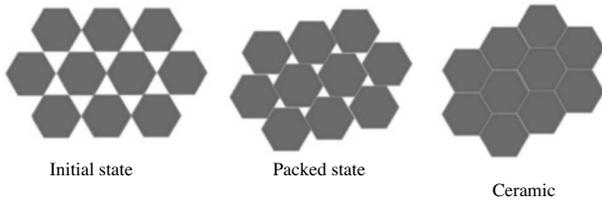


FIG. 2. Model of the densification of a ceramic composed of crystals with a cubic structure.

3. Shape homogeneity

This is necessary to achieve dense packing. Denser packing of the particles reduces the distance that the substance needs to be transported during sintering and accordingly increases the packing rate of the ceramic. If the particles have identical orientation of the crystallographic axes relative to the particle shape in this case, the shrinkage of such composites during drying and sintering will be isotropic. These concepts were applied to the description of the process of sintering cubic nanocrystals.¹⁴ Akchurin *et al.* studied the structure and the deformation specifics of the initial nanoceramic and concluded that the angles at the vertex, formed by the boundaries of three grains in the ceramic, equal about 120°. This angle is characteristic of the contact of twins in the {112} direction on the {111} face of the original cubic crystal. Similar twins are formed when cubic crystals are grown. According to the twinning model proposed by the authors, the structure of the ceramic, the orientation of the grains, and a decrease of the pores occurs during plastic deformation of the sample. This process mainly occurs at the stage of cold pressing of the blank at a pressure of 100–200 MPa before the subsequent vacuum sintering. A diagram of the process is shown in Fig. 2. This model contradicts the most widely held opinion, that spherical particles should be used to obtain a pore-free ceramic and that their packing should be maximized during formation. It is assumed in fact that the spherical particles are formed by cubes inscribed in a sphere. The initial loading during pressing is sufficient for plastic deformation of even such low-plasticity crystals as $Y_3Al_5O_{12}$. Healing of the pores occurs by the transfer of substance, accompanied by rotation of the lattice. The process responsible for forming a pore-free ceramic is thus analogous to the twinning of crystals.

4. Particle agglomeration

Agglomeration results in inhomogeneous packing, followed by inhomogeneous sintering. As a result, internal pores and cracklike cavities¹⁵ are formed in the ceramic sample. The character of the agglomeration can be separated into two types. With mild agglomeration, the particles are held together by weak van der Waals forces. With strong agglomeration, the particles are connected to each other by bridges composed of strong chemical bonds. Powders for sintering must possess the minimum degree of agglomeration, as far as possible avoiding strong agglomeration. To demonstrate how agglomeration affects the porosity of a ceramic, Fig. 3 shows how the density of a ceramic based on

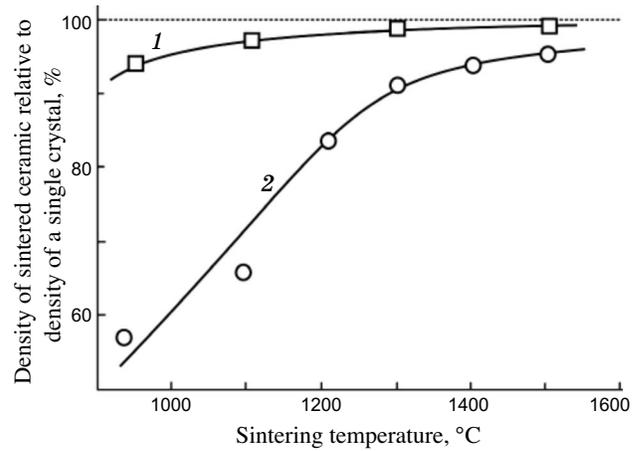
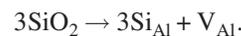


FIG. 3. Density of a sintered ceramic based on zirconium dioxide stabilized with yttrium oxide, relative density of a single crystal as a function of the sintering temperature for 1 h.¹⁶ 1—nonagglomerated powder, 2—agglomerated powder.

stabilized zirconium dioxide depends on the sintering temperature.¹⁶ Although the sintering kinetics depends on many factors, including the particle size, their packing density, the pressure and composition of the atmosphere, etc., the example given here nevertheless shows that nonagglomerated powders make it possible to achieve higher density of the ceramic at lower temperature.

5. Examples

Some impurities are often responsible for the process of excitation transport and variation of the strength of the ligand field around the luminescence center. Such impurities should therefore be avoided, and this general rule is applicable to any laser materials. As applied to ceramic, the influence of impurities is not restricted to these. Most impurities are either dissolved in the main substance or form insoluble inclusions. Dissolved impurities change the concentration of intrinsic defects in the matrix and accordingly change, for example, the diffusion coefficients of the main components. The values of the latter are important for the sintering process. A well-known example is the addition to aluminum oxide of small amounts (about 100 ppm) of MgO or SiO₂, which make it easier to obtain a transparent ceramic.¹⁷ The explanation of the role of additives of isovalent oxides to the sintering kinetics reduces either to an increase of the self-diffusion coefficient when an impurity is introduced or to a decrease of the surface energy of the grains in the presence of a foreign phase. The introduction of additives in the form of a substituent impurity also results in the generation of defects. For instance, when silicon dioxide impurity is introduced into the aluminum oxide sublattice, a reaction occurs according to which one vacancy is formed on each of three introduced silicon ions into the aluminum sublattice; i.e.,



The SiO₂ impurity introduced into the ceramic during sintering, followed by slow cooling, can precipitate out in the

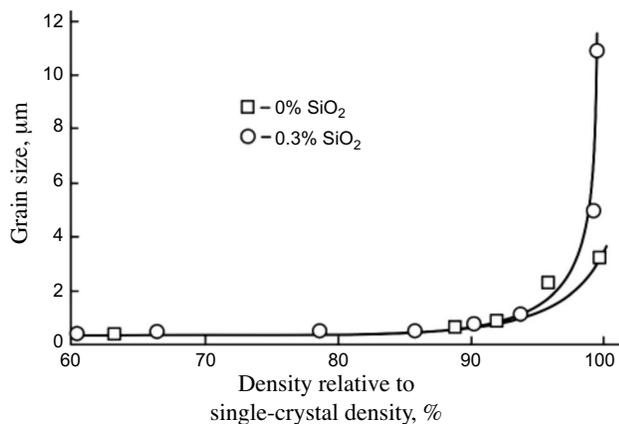


FIG. 4. “Road map” of sintering of a YAG ceramic.¹⁹

form of glass at the grain boundaries and can play the role of scattering centers that degrade the transparency of the ceramic.¹⁸

The influence of SiO₂ impurity on the sintering process of a ceramic based on yttrium aluminum garnet can be understood by considering the sintering road map shown in Fig. 4.^{19,20} The grain-size—ceramic-density trajectory characterizes the ratio of the packing rate of the ceramic to the growth rate of the grain.

In the opinion of Maotre *et al.*,¹⁹ depending on the experimental conditions and the SiO₂ concentration, three types of microstructure are observed: a porous material (relative density from 60 to 90%) with a submicron grain, a ceramic with closed pores and density from 90 to 97% with micron grains (on the average 2 μm) and packing density, and a ceramic with mean grain size greater than 3 μm . At 1973 K, the mean grain size remains of the order of 5 μm in a ceramic doped with SiO₂, whereas it increases to 11 μm in the pure ceramic. This means that a SiO₂ dopant increases the packing rate of the ceramic relative to the growth rate of the grain, being a growth inhibitor of the grain and promoting the more homogeneous microstructure needed to obtain a transparent ceramic. The packing rate of the undoped ceramic is limited by the diffusion process of rare-earth ions along the grain boundaries. When SiO₂ is added to the mix, the growth of the crystals and the densification of the ceramic, in the authors’ opinion, occur by the liquid-phase sintering mechanism. The sintering rate increases with the growth of the impurity concentration, as a result of the increase of the transfer rate of the substance through the liquid phase and the decrease of the contact density of the grains according to the solid–solid type.

6. Phase homogeneity

The powder must be single-phase and must consist of that phase that is expected to be obtained when the ceramic is sintered. As applied to a laser ceramic, one should also add a uniform distribution of impurity rare-earth materials (REMs) over the starting nanoparticles, in order to prevent the segregation of REM ions from affecting the laser properties of the ceramic.²¹

7. Maximum density of the starting sample

A sample fabricated from the starting powder must contain the minimum number of pores. Macro- and mesopores, if they are present in the sample, create problems during sintering.

8. Minimum weight loss during sintering

In the process of heating the ceramic material to a high temperature, the surface of the powder continuously degrades until the pores are completely closed. The pressure of the gas captured by the pores is directed against the compressive pressure of the sintering and therefore prevents the pores from completely disappearing. The nature and composition of the trapped gases depend on the production method and thermal prehistory of the powder. For example, methane, formed when methanol is used as a wetting medium in a ball mill, is present in the powder when it is sintered all the way to a temperature of 1000 °C.²² Since the oxides of aluminum, yttrium, neodymium, etc. tend to hydrate and carbonize the surface, water and carbon dioxide can be completely removed only by heating to 1200 °C. The adsorption and desorption processes are substantial for nanopowders with a highly developed surface. For them, it is important to maintain high purity of both the reagents and the ambient medium, as well as controlled storage conditions.²³ An additional annealing stage to remove volatile impurities before the finishing stage of sintering the nanopowders substantially improves the quality of the optical ceramic.

C. Methods of synthesizing nanopowders and preparing the mix for a laser ceramic

Two main approaches to the synthesis of the starting powder-precursors are used to fabricate a transparent ceramic:

- the dry or mechanochemical method,
- the wet or another chemical method of synthesizing the starting materials.

1. Mechanochemical synthesis

The essence of the mechanochemical synthesis of the precursors consists of grinding a mix of oxides in a ball mill. It was at first assumed that the use of direct sintering of powders of the starting oxides without intermediate synthesis of garnet gives no possibility of synthesizing ceramic samples of optical quality. At the same time, such a synthesis method possesses simplicity and the possibility of implementing it in commercial production. The most impressive results were attained by Ikesue *et al.*²⁴ A diagram of the process of ceramic synthesis that they developed is presented in Fig. 5. An important feature of this process is that the authors monitored the pore size before the samples were sintered, decreasing it by isostatically pressing the granules at room temperature. The density of the pressed samples was 55% of the theoretical value, with a mean pore size of 10 nm.

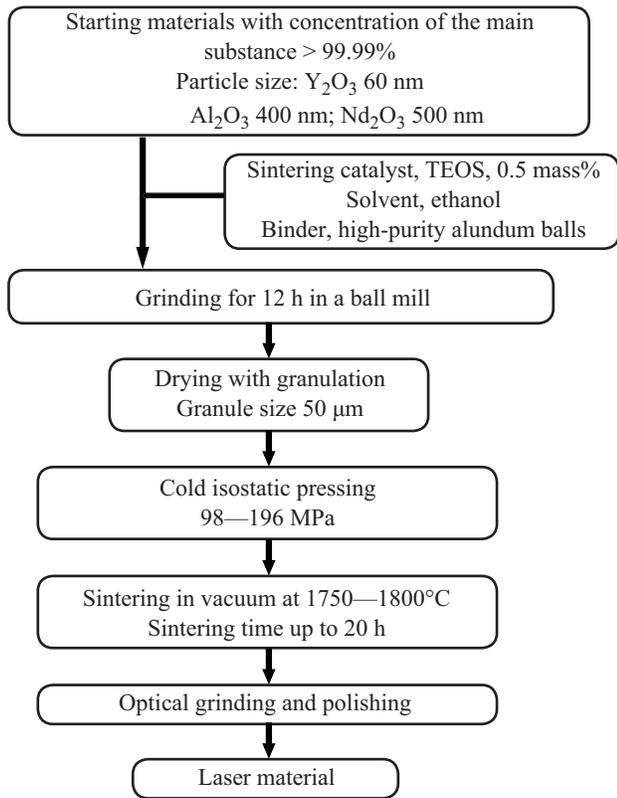


FIG. 5. Diagram of a mechanochemical method of preparing a mix and synthesizing a laser ceramic.²⁴

The process of grinding and obtaining the starting material is as follows:² High-purity yttrium, aluminum, and neodymium oxides (99.999–99.9999) with a particle size from 60 to 400 nm are used as the starting substances. The powders are mixed in the stoichiometric ratio of YAG, and ethyl alcohol and about 0.5 mass% of tetraethoxysilane (TEOS) is added to them. The mix was ground in a ball mill with balls made from high-purity alundum for 12 h, and the necessary quantity of an organic binder was also added to it. A similar method was later successfully used to obtain highly doped (with up to 4% Nd) ceramic.^{25,26}

The process of grinding the mix of powders in a ball mill is not simple mechanical crushing of the components. The processes that occur during grinding are shown schematically in Fig. 6.²⁷ They include both the process of grinding

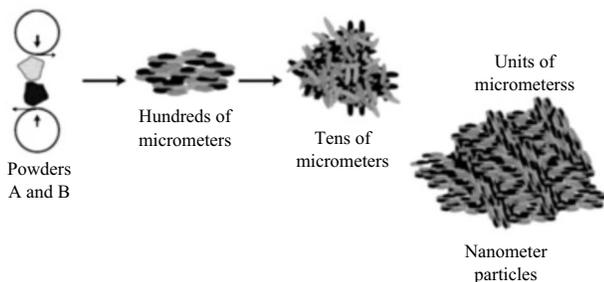


FIG. 6. Sequence of transformations of a mix when it is ground in a ball mill.²⁷

each of the phases and the process of mixing and combining them into agglomerates.

In the course of prolonged grinding, the size of both reagents decreases in time approximately exponentially.²⁸

As shown in Fig. 6, as a result of impacts, when the balls and the powder collide, the particles of the latter break up and then again coalesce into various agglomerates. This sequence of breakup and formation of fragments takes place during the entire grinding process. The mixed particles interact by diffusion and thermal action upon impact. The number of impacts that the particles of both components experience is very great and can reach thousands per second. The repeated impacts will result in the formation of folded structures in which the components alternate. With time, the folded structure will become smaller and smaller until a structure of nanometer scale is obtained. As a result of prolonged grinding, the reactivity and sinterability of the YAG powders very strongly increase.^{29,30} After being ground for 20 h, the powders consist of individual oxides, but their crystalline structure is very strongly degraded. In this case, the separate particles of the oxides are strongly sintered with each other, forming agglomerates of a composition close to that of the garnet. It is the metastable state of the particles of the individual oxides after grinding that makes it easy for them to chemically interact at elevated temperature. The formation of a well-formed garnet phase begins at 1000 °C. The rapid growth of garnet grains and the obtaining of single-phase powders are observed at a temperature of about 1300 °C.³¹ At the same time, with standard solid-phase synthesis of YAG from the oxides, it forms at a temperature of 1500–600 °C.

After grinding, the slip is sprayed and dried to obtain spherical granules that have a homogeneous composition. The granule size has critical significance for consequently obtaining samples with low porosity.³² The size distribution of the granules is controlled by the drum-rotation rate in the device for spray drying. The size of the spherical granules usually lies between 50 and 100 μm, with a mean size of the individual pore in them of several micrometers.

The granulated powder is pressed into plates, disks, or rods in an ordinary metallic compression mold. The blanks are then subjected to cold isostatic pressing at a pressure of 98–196 MPa. The density of the resulting sample is from 50 to 55% of the density of the monolithic material.

After pressing, the blank was heated to eliminate the organic binder. A monolithic transparent sample is obtained after sintering in vacuum (10^{-3} Pa) at 1750 °C for about 20 h. The ceramic contains none of the optical inhomogeneities, including birefringent regions, that can be seen, for example, in single-crystal YAG. The refractive-index inhomogeneity over the sample is about 10^{-5} , and this is evidence that the ceramic is of high optical quality. The technological process does not impose any fundamental limitations on the size and shape of the sample.

A similar method is used to obtain a transparent YAG ceramic.^{33–35} The difference from the mechanochemical method described above is that yttrium oxide, chemically precipitated from a solution of yttrium nitrate, is used. A

solution of ammonium bicarbonate was used to obtain an insoluble precipitate (a precipitant). Ammonium sulfate, playing the role of dispersant, was also added to the yttrium nitrate solution. After the precipitate was aged at room temperature for 2 days under conditions of continuous mixing of the solution, the yttrium carbonate precipitate was filtered and repeatedly rinsed with deionized water. The aged yttrium carbonate precipitate was crystalline but consisted of poorly formed crystals. The precipitate was then heated at 500–200 °C for 4 h at a heating rate of 5 K/min. Yttrium oxide begins to form at a temperature of about 500 °C. The decomposition of yttrium carbonate is complete at 700 °C, and well-formed crystals of cubic yttrium oxide are observed after heating at 1100 °C. The yttrium oxide powders obtained in the presence of the dispersant are homogeneous, with a narrow size distribution of the particles and a mean grain diameter of about 60 nm. Powders synthesized without a sulfate additive were strongly agglomerated, and this made it hard to use them for the subsequent synthesis of ceramic. The authors explain the action of the sulfate as a dispersant as follows. The yttrium carbonate surface in solutions with high pH is positively charged. The sulfate ions are specifically adsorbed on the surface of the carbonate precipitate. Since the yttrium sulfate decomposes at a much higher temperature than the carbonate, its presence on the surface prevents sintering, because of interparticle diffusion. The yttrium oxide thus obtained is mixed with commercial aluminum oxide and is ground in a ball mill for 5 h in a medium of ethanol. The subsequent process to obtain the ceramic does not differ from the processes used by other authors.

The mechanochemical method of synthesis was also successfully used to synthesize YAG ceramic co-doped with neodymium and chromium.³⁶

2. Chemical precipitation of hydroxocarbonates^{10,11,37–39}

Precipitation in the form of nanoparticles of a mix of hydroxocarbonates, followed by synthesis of nanometer particles, was a very applicable method for obtaining not only garnet but also transparent ceramic based on other refractory oxides with a cubic lattice— Y_2O_3 , $YGdO_3$, Sc_2O_3 , Lu_2O_3 ,^{40–42} and erbium-doped yttrium oxide,⁴¹ as well as yttrium aluminum garnet simultaneously doped with chromium and calcium.⁴²

A diagram of the carbonate method of producing a ceramic based on yttrium aluminum garnet is shown in Fig. 7. Chlorides or nitrates dissolved in water in stoichiometric ratio are used as the starting solutions. This solution is added in drops to the precipitant—ammonium bicarbonate. The precipitate is filtered, rinsed, and dried for 2 days at 120 °C. The resulting precursor consists of 10-nm particles. The YAG phase using the bicarbonate method is formed at low annealing temperature of the precipitate—for example, according to the data of Ref. 43, at 300 °C. Pure yttrium aluminum garnet powder is obtained by heating the precursor at 1200 °C.

Other reagents such as urea, solutions of which are hydrolyzed at elevated temperature by changing the reaction of

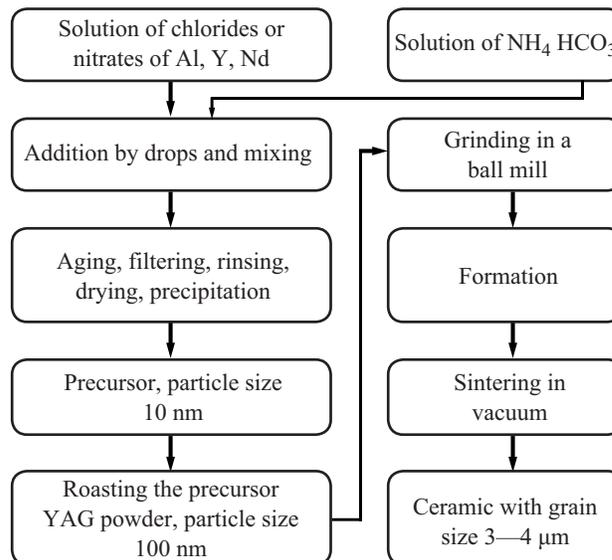


FIG. 7. Technological process of synthesizing a YAG ceramic by the bicarbonate method.³⁸

the medium from acid to alkali and by promoting the precipitation of hydroxides,⁴⁴ can also be used as a precipitant. The choice of a precipitant is a fundamental question, since it is obvious that not only hydroxycarbonates but also nanocrystalline precipitates of hydroxides, oxalates, etc. can be used as precursors. Li *et al.*⁴⁵ compared the results obtained by using ammonium bicarbonate and hydroxide as a precipitant. When there is interaction with ammonium bicarbonate, aluminum hydroxide can be precipitated in the form of boehmite $AlOOH$ or dawsonite $NH_4Al(OH)_2CO_3$. In order to avoid the formation of a gellike hydroxide, Ikesue *et al.*²⁴ used a concentrated solution of ammonium bicarbonate with a concentration of 1.5 mol/L and, for comparison, a solution of ammonium hydroxide with the same concentration. Two versions of the precipitation are possible. A solution of the precipitant can be added in drops to a solution of the salt or the reverse—a solution of the salt can be added to a solution of the precipitant. The latter method is preferable when multicomponent mixes are being obtained, since it provides more uniform co-precipitation. The use of ammonia liquor as a precipitant results in the formation of a gellike precipitate of aluminum hydroxide, which undergoes shrinkage of up to 70% during drying. The resulting precursor is strongly agglomerated and is hard to pulverize with a mortar and pestle. The precipitate obtained by adding ammonium bicarbonate to the nitrate mix has a nonhydroxide nature. When it is dried, its volume decreases by only 10%, and it is then easy to grind with a pestle. The composition of the precipitate is the result of competition between the hydroxide and carbonate anions, and its composition is approximately expressed by the formula $NH_4Al(OH)_2CO_3$. On the other hand, yttrium easily forms both a neutral and a basic carbonate.

Regardless of the precipitant's composition, the precipitates remain amorphous when they are heated to about 850 °C. The precursors completely break down and achieve a constant weight at 900 °C. The precursors then behave

differently. When the hydroxide precipitate is heated at 800–900 °C, ternary phases form—yttrium aluminum perovskite and yttrium aluminum garnet.⁴⁶ When the heating temperature is increased further, the composition of the crystals approaches the garnet composition. At the same time, the precursor obtained by the carbonate method crystallizes at 900 °C in the form of pure garnet with no formation of intermediate phases. As the temperature is increased further, growth and improvement of the crystallinity of the precursor are observed. Intense crystal growth begins for all types of powders, beginning at 1100 °C.

The influence of the precipitant is also considered in Refs. 47 and 48. The authors of the former paper investigated the role of the precipitant in forming nanopowders of neodymium-doped lutetium oxide. Five compositions of the precipitants were taken: ammonium oxalate, ammonium bicarbonate, a mix of ammonium bicarbonate and ammonium hydroxide, ammonium hydroxide, and urea. All the precipitants were added to the mother solution of lutetium and neodymium nitrates at a rate of 3 mL/min. After precipitation, the pH of all the solutions was held approximately constant at a level of 8–9. From the results of an analysis of the particle sizes obtained when the precipitates were heated, the authors also arrived at the conclusion that the smallest agglomerated powders are obtained when ammonium bicarbonate is used as the precipitant.

The appearance of particles with sizes to 1000 nm is explained by strong agglomeration, most characteristic of precipitation by ammonium hydroxide and urea.⁴⁷ The highest dispersivity of the powders with a mean particle size of 50 nm was achieved by depositing the precursor with the help of a mix of ammonium hydroxide and bicarbonate. The same powders demonstrate the best sinterability—their sintering begins at a lower temperature and is accompanied by greater shrinkage. Meanwhile, the addition of the sulfate ion, which inhibits the growth of nanocrystals, promotes the obtaining of weakly agglomerated crystals when urea is used as a precipitant.⁴⁹ The addition of an anionic surfactant also promotes the obtaining of more finely dispersed particles of YAG.⁵⁰

With the carbonate method of precipitation in the version of hydrothermal synthesis, garnet nanopowder can be obtained even at 300 °C.⁵¹ A hydroxycarbonate precipitate obtained ahead of time is later recrystallized in a water-alcohol solution at a pressure in the autoclave of up to 10 MPa. The addition of ethanol promotes the formation of the YAG phase under milder conditions than in a water solution. A single-phase product consisting exclusively of garnet is obtained by holding the solution at 300 °C for 1 h. The resulting crystals have a mean size of about 30 nm and are characterized by a narrow size distribution and fairly perfect crystalline structure.

Two approaches to the synthesis of the starting powders for sintering—the mechanochemical method, which characterizes the traditional synthesis of the ceramic, and the use of chemically precipitated precursors—were compared under identical conditions to see if either of them have an advantage for obtaining a high-transparency ceramic.⁵² Bravo *et al.*

used ammonium bicarbonate as a precipitant from a nitrate solution. They used sintering to obtain ceramic samples of identical composition. The main difference between the two methods was that the ceramic's sinterability and grain size is greater for the chemically precipitated precursor. Possible ways to increase the density of the ceramic are

- by introducing additives that make sintering easier into the chemically precipitated precursors,
- by applying a slip method or cold isostatic pressing to increase the initial density of the blank or hot isostatic pressing at the concluding stage of the sintering,
- and by optimizing the sintering stage.

3. The citrate-gel method

It is assumed that, to synthesize a transparent YAG ceramic, it is necessary to use nonagglomerated powders that consist only of the YAG phase and contain no impurities of other phases, such as yttrium aluminum perovskite $YAlO_3$, the monoclinic phase $Y_4Al_2O_9$, or Al_2O_3 . The citrate-gel method has the advantage that the garnet phase is formed at a comparatively low temperature.⁵³ To obtain the starting gel, a mix of aluminum and yttrium nitrates in the stoichiometric ratio of garnet is dissolved in water, and a 2 mol/L solution of citric acid with a 1:3 ratio of nitrates to citric acid is added to the solution. The solution is evaporated at 80 °C, and the resulting gel is dried at that temperature in vacuum for 24 h. Powder for subsequent sintering is obtained by thermally decomposing the gel at 600 °C for 6 h. There is virtually complete decomposition of the gel at this stage. In the dynamic heating regime, total decomposition of all the intermediate phases, including the carbonate phases, is completed at 815 °C. The beginning of the formation of the YAG phase is fixed at 800 °C. It becomes the only one during annealing, beginning at 1000 °C, and is highly perfect at 1200 °C. With prolonged isothermal annealing for 6 h, the garnet phase is the only one and is already fairly complete at a temperature of 900 °C. The authors used YAG powder obtained by roasting at 900 °C as a precursor for the sintering of ceramic. To do this, the powder was ground in a mill to a particle size of about 0.55 μm , adding to it 652 ppm of zirconium dioxide as a ceramic-densification catalyst and 131 ppm of silicon dioxide as an dopant that improves the sinterability. Sintering of the powder in air was observed beginning at 1400 °C, and samples with relative density 95.2% were already obtained at 1600 °C.

4. Obtaining nanopowders by self-propagating synthesis^{54,55}

The essence of the method consists of using self-maintaining oxidation–reduction reactions as a heat source for local heating of the required mix of starting substances and the synthesis of the final product that occurs in the reaction zone. The advantages of the method consist of its simplicity, the low temperature of synthesis, and the homogeneity of the starting reaction mix. Homogeneity of the starting mix is ensured by using gel in which a self-maintaining reaction is induced as an intermediate product. Nitrates are

ordinarily used as oxidants, and organic ligands—often citric acid—as reductants. The authors of the cited papers used various reductants—citric acid, EDTA, glycine, and glycol and various methods of drying the gel to obtain YAG doped with 2 mol% of neodymium. When the gel is heated at the first stage (between 80 and 200 °C), the alcohol and moisture residues contained in the gel evaporate. Pyrolysis of the organic components and their heating under the action of the oxidant are initiated at a temperature of from 200 to 540 °C. The most substantial weight loss (more than 50%) occurs in this temperature region, and a large quantity of gas is formed—CO₂, NO₂, and H₂O. The garnet-formation process occurs at a temperature of from 600 to 1100 °C and is accompanied by a weight loss of from 5 to 10%. The temperature at which all chemical processes are complete depends on the nature of the reductant and lies in the limits from 926 °C for a gel with citric acid to 962 °C for a gel with glycine. A substantial feature of the method is that a well-formed garnet phase is obtained at an annealing temperature below 1000 °C. The resulting nanoparticles are prolate agglomerates from 150 to 500 nm long and from 30 to 150 nm in diameter. According to x-ray diffraction data, the samples obtained using citric acid consisted exclusively of the garnet phase and did not contain any other phases.

Intermediate between the self-sustaining synthesis and citrate methods is the Pechini method.⁵⁶ In this method, because of the esterification reaction between citric acid associated with the metal ions and ethylene glycol, a polymer is formed in which the aluminum and yttrium atoms are distributed as homogeneously as possible. The distribution remains uniform even after the organic components of the polymer are burned off, because of which the diffusion length decreases upon sintering. An advantage of the method is also that nanocrystals that have a fairly perfect crystal lattice are formed at a low temperature. The Pechini method was used by Hreniak *et al.*⁵⁷ to synthesize YAG nanopowders doped with neodymium. The authors used a mix of aluminum and yttrium nitrates dissolved in an aqueous solution of citric acid and ethylene glycol with a molar ratio of 3:5:10:4 as the starting salts. The solution was evaporated at 90 °C until it completely polymerized. When the gel is roasted, the final loss of water and decomposition of the nitrates occur in the temperature interval from 100 to 600 °C. The weight loss of the gel when it is heated to a temperature of 600 °C is about 80%. The garnet crystal lattice forms at a temperature below 900 °C, while the final loss of carbon occurs at 1000–1100 °C.

The nanopowders synthesized by the Pechini method are agglomerated. The agglomerates formed when the gel is roasted are characterized by a large pore volume, probably associated with high outgassing during synthesis.^{53,58} Figure 8 shows the size distribution of the garnet particles after roasting and after the powder is subsequently ground in a ball mill.⁵³

The roasted powder is thoroughly ground because the large volume fraction of pores prevents it from being strongly agglomerated. Grinding already reduces the mean particle size from 15 to 1.4 μm in 20 min. When grinding is

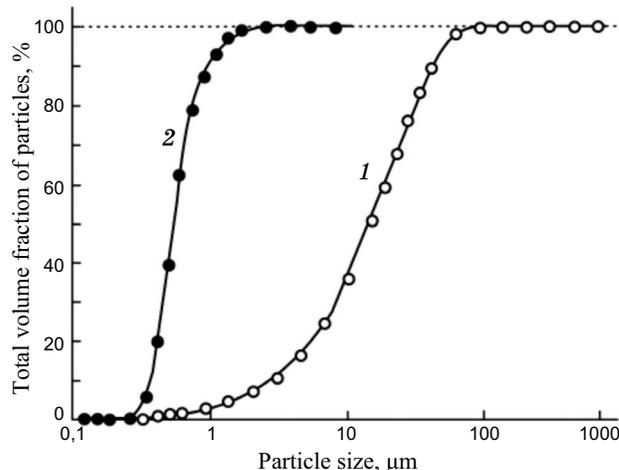


FIG. 8. Distribution of garnet particles over size after roasting and subsequent grinding in a ball mill for 2 h.⁵³ 1—Immediately after roasting, 2—after grinding the roasted powders.

kept up for 2 h, the mean particle size reaches the minimum value of 0.55 μm. The character of the particle distribution in size also varies during grinding. If it is wide—from 0.3 to 100 μm—in the original powder, the distribution after grinding is limited to the region from 0.3 to 2 μm.

After pyrolysis at 900 °C for 16 h, the size of the YAG crystals ranges from 30 to 50 nm. Ceramic samples with transmittance 52% at a wavelength of 1064 nm were obtained from the synthesized powders by pressing at a temperature of 450 °C and a pressure from 2 to 8 GPa,⁵⁹ and this corresponded to an attenuation coefficient of 13.6 cm⁻¹. A study of the microstructure showed that there are uniformly distributed fine pores between the separate grains. As the pressure varied from 3 to 8 GPa, the density of the samples increased from 76 to 98% of the theoretical value, whereas the density was 51% of the theoretical value for the initial pellets pressed at low pressure.

5. Laser vaporization^{60,61}

The method of laser vaporization of a target with the radiation of a CO₂ laser was used to obtain weakly agglomerated powders. Powders of yttrium and neodymium oxides were used as the material. The powder yield was 24 g/h on the average for a light-energy consumption of 90 kJ/g. The powders included two fractions: the main fraction, consisting of spherical particles with a mean diameter of 10 nm, and a small fraction of spherical particles from 0.2 to 2 μm across. The authors associate the generation of the large particles with the expulsion of liquid from the laser crater. The large particles are easily separated from the main fraction by sedimenting the powder in isopropyl alcohol.

Oxide nanopowders of the monoclinic modification were obtained by condensation. The ceramic samples obtained from the given powders were shattered during sintering because of the large volume change with polymorphic transformation of the monoclinic oxide into the cubic oxide. To sinter the ceramic without forming cracks, the nanopowders obtained by condensation were annealed at 800–850 °C to

obtain the cubic modification of neodymium-doped yttrium oxide. Annealing at these temperatures for 10 h produced virtually complete transformation of the monoclinic yttrium oxide into cubic. The modified powders were pressed by magnetic-pulse pressing at room temperature with a pressure amplitude of 0.3 GPa into three-millimeter disks from 15 to 32 mm in diameter. The relative density of the pellets was about 50%. The pellets were next sintered in vacuum (10^{-5} Torr) at a temperature of up to 1900 °C. A dilatometer measurement of how much the sample shrinks during synthesis shows that the sintering process already begins at temperatures above 600 °C, and fairly perfect grain boundaries are formed in the ceramic when they are annealed for 10 h at 1450 °C. Nevertheless, annealing for 10 h at 1750–1900 °C was needed to completely remove the pores. A substantial decrease of porosity of the samples from 1.2 to 0.03% occurs as the sintering temperature is increased from 1543 to 1900 °C.

6. The sol-gel method

An undoubted advantage of this method is that crystalline phases of complex composition can be obtained at comparatively low temperatures, ensuring nanosize crystals. For example, after separately obtaining sols of aluminum, yttrium, and ytterbium oxides and mixing them, Wang *et al.* already obtained the garnet phase with a narrow distribution over size around a mean value of about 100 nm when they roasted the mix at 850 °C.⁶² From the viewpoint of obtaining a pore-free laser ceramic, the main problem of the sol-gel method is that strongly agglomerated powders are obtained as a result of the process.⁴⁵ Meanwhile, Mathur *et al.*⁶³ showed that the correct choice of the precursors has great significance when the sol-gel method of synthesizing powders is used. They obtained high-quality YAG ceramic when they used rare-earth alkoxides as precursors. When they used this method, the YAG phase was the only one, beginning with a roasting temperature of 700 °C. A poreless ceramic was obtained in 1 h at 1500 °C when powder predispersed by ultrasound was sintered.

D. The process of preparing and sintering the ceramic

One way to prepare a ceramic for sintering is the slip method. As starting powders, Kopylov *et al.*⁶⁴ used powders obtained by coprecipitation of yttrium, aluminum, and neodymium hydroxycarbonates from aqueous solutions of yttrium and neodymium nitrates and of aluminoammonium alum by an aqueous solution of ammonium bicarbonate. The specific surface of the powders was reduced from 40 m²/g to 3 m²/g by increasing the annealing temperature from 950 to 1300 °C. To break up the agglomerates, the authors used an agate mill with agate balls. The grinding was done in the presence of 0.3–0.5% of tetraethoxysilane. The necessary quality of the grinding was confirmed by the high stability of the slip—the appearance of a precipitate in the lower part of a glass cylinder with slip was observed after several hours of settling. This corresponded to obtaining weakly agglomerated YAG powders with a particle size from 60 to 200 nm. As a result of hydrolysis of the tetraethoxysi-

lane, some quantity of silicon dioxide was formed, which subsequently served as a catalyst for sintering the ceramic. To prepare the slip, the authors used ammonium polyacrylate as a deflocculant. The use of a deflocculant made it possible to obtain a slip with a concentration of dry substance of up to 40 vol%, and the behavior of the slip was Newtonian in this case.

The low viscosity of the slip and its Newtonian nature promoted obtaining the densest packing of the particles when the sample was cast in a porous compression mold. Newtonian behavior of the slip is observed only in the final stage of the process in the compression mold, when dewatering of the slip becomes appreciable.

It follows from the theory of sintering (see, for example, Ref. 13) that, with the densest particle packing, when the dihedral angles of the pores are great, all the pores in the structure are unstable relative to their collapse during sintering. Any residual porosity of the ceramic that can be observed after sintering is associated with the existence of packing defects in the blank, in which the shape of the pores substantially differs from the shape of the interparticle pores. To improve the packing of the starting blanks, Kopylov *et al.*⁶⁴ used the method of casting the blanks with pressing in a porous compression mold. The diameter of the mold was 27 mm. Aluminum oxide from 3 to 5 mm thick was used as a porous medium. The porosity of the membrane was 470 nm, and its thickness was 100 μm. Samples from 1 to 8 mm thick were obtained as a result of the pressing. The pressure of the pressing was 200 MPa. After being pressed, the samples had a density greater than 60% of the density of a single crystal, which is close to the densest packing density of spherical particles.

The preforms were initially annealed in air at a temperature of 1100 °C for 2 hr to completely eliminate organic residues. After this, the samples were annealed in vacuum (10^{-5} Torr) at a temperature of 1700–800 °C for from 3 to 20 h. The furnace was heated at a rate from 1 to 3 K/min. The transmittance of samples 1.5 mm thick was 80% at a wavelength of 1.06 μm. On the resulting ceramic samples, the authors obtained a mean output power of 0.6 W at a wavelength of 1064 nm with a pulse-repetition rate of 50 Hz.

A comparison of the slip method of producing a laser ceramic and the method that uses hot isostatic pressing is given by Esposito and Piancastelli.⁶⁵ It is important that, for all the experiments, the authors used a mixture of oxides obtained by virtually the same method of grinding the powders in the presence of 0.3–0.5 mass% of the dispersant and an additive of tetraethoxysilane. The ceramic samples subjected to cold isostatic pressing had higher transparency than the samples obtained by the slip method. In the case of the slip method, more prolonged grinding of the powders makes it possible to obtain smaller crystals, but the viscosity of the slip becomes too high, and this prevents dense packing of the particles when the liquid is filtered. A comparison of the efficiency of hot isostatic pressing for 2 h at 1750 °C and a pressure of 200 MPa for samples prefabricated by pressing dry powders and samples prepared by slip casting was car-

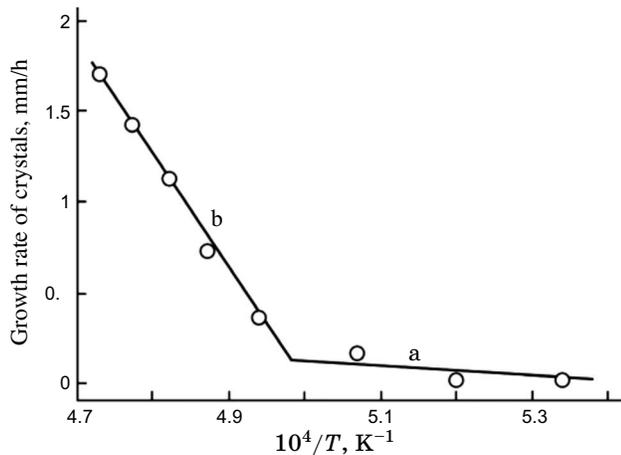


FIG. 9. Growth rate of a grain in a YAG ceramic vs sintering temperature in vacuum.²⁴ (a) Normal-growth region, (b) abnormal-growth region.

ried out by Lee *et al.*⁶⁶ They found that isostatic pressing is most effective for the samples prepared by the slip method. In ceramic samples that use the given method of preparing the starting components, macropores greater than $1 \mu\text{m}$ across are absent, unlike samples for which pressing of dry powders was used. The use of hot isostatic pressing has one more positive effect—it makes it possible to decrease the quantity of SiO_2 added to the powder to improve its sinterability. Along with this, when hot isostatic pressing of a ceramic sample is used with no isolating shell, the compressing gas (argon) is dissolved in the ceramic, which is promoted by the presence of silicon dioxide in it. With subsequent vacuum annealing, the argon is given off in the form of bubbles surrounded by the aluminosilicate component.⁶⁷ As a result, first, the sample's transparency is reduced and, second, the neodymium is segregated in the region around the pores.

An important advantage of the slip method is the possibility of avoiding the stage of not only cold but also hot isostatic pressing—one of the most technologically complex and expensive stages. According to Ref. 68, the correct preparation of the mix makes it possible to obtain samples of ceramic spinel of optical quality by using the method of uniaxial hot pressing. Using a press with a force of 250 Tonne, ceramic samples were obtained with a size of 14 in. \times 14 in.

Ikesue *et al.*²⁴ investigated in detail the process of sintering a mix obtained mechanochemically in vacuum in the high-temperature region. They measured the growth rate of the grains in a wide temperature interval—from 1600 to 1850 °C—and found that the temperature dependence of the growth rate consists of two parts (Fig. 9). Beginning at a temperature of about 1700 °C, the growth rate of the grains strongly increases. The authors called this temperature region the abnormal growth region. The abnormal growth rate is 1.7 mm/h at a temperature of 1840 °C. If they use a piece of single-crystal YAG as a blank at these temperatures, the ceramic sample transforms with time into a single crystal. To suppress the growth of crystallites when sintering, Chen *et al.*⁶⁹ used two-stage sintering: rapid heat-

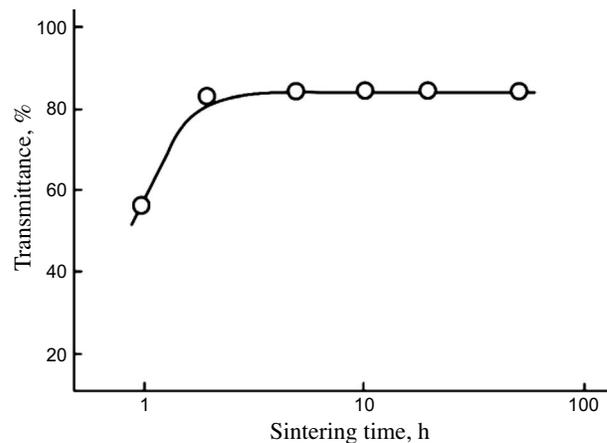


FIG. 10. Transmittance of a YAG ceramic at a wavelength of $1 \mu\text{m}$ vs sintering time in vacuum at 1750 °C.²⁴

ing in vacuum to a high temperature (about 1800 °C) and moderately fast cooling to a lower temperature (from 1500 to 1700 °C), holding at that temperature for 10 h. As a result, denser and more transparent samples were obtained than with one-step heating.

The sintering time in vacuum is important for obtaining samples of high optical quality. Figure 10 shows how the transmittance of a sample 3 mm thick depends on the heat-treatment time at 1750 °C. The transmittance of the sample reaches the theoretical value of 84% after two hours of sintering. Further sintering reduces the losses to scattering, and at least 10 h are necessary to obtain a ceramic of optical quality. In this case, the scattering coefficient is less than 0.9%/cm, and the images of objects are seen through a ceramic several centimeters thick. The ceramic consists of grains about $50 \mu\text{m}$ across, with very distinct intergrain boundaries and a porosity of about 1 vol.ppm. The difference in the regimes for preparing the ceramic has a substantial influence on the light scattering in it.¹⁸ Light scattering is what differentiates a ceramic from a single crystal of the same composition. It is the consequence of the presence of pores and grain boundaries in the ceramic. The losses to scattering in ceramic samples with small pore content and low silicon oxide concentration are almost equal to the losses in a single crystal. This means that the optical losses on perfect grain boundaries are negligible. The SiO_2 impurity introduced to suppress grain growth during sintering is concentrated at large concentrations at the grain boundaries during cooling. This effect is appreciable when the ceramic is cooled slowly after sintering and is absent when it is cooled rapidly. Impurity segregation at a grain boundary makes the latter optically imperfect and results in the appearance of the light-scattering effect at the grain boundary.

The optimum technological process, which, on one hand, would ensure a high-quality laser ceramic and, on the other hand, would be economically efficient, has not yet been developed. The main critical stages of the process are understood—the requirements on the starting powders in purity, in the size of the nanocrystals, and in the degree of their agglomeration. The stage of sintering the sample, prepacked

in one way or another, in high vacuum at a temperature of about 1700–750 °C of the predegassed sample, is also indispensable. The formed sample must have a density of about 55% of the theoretical value before sintering and must not contain pores of micrometer size. The question of whether isostatic pressing is indispensable remains open,⁶⁸ since it is possible that, when the processes for obtaining powders and forming a blank from them are further optimized, isostatic pressing, both cold and hot, may become unnecessary.

III. CONCLUSION

Laser ceramic is a new class of active laser media, commercially implemented in the last 10–15 years, which combines the advantages of both laser crystals and laser glasses in one material. The technology for producing laser ceramic is the result of incorporating new methods of synthesizing the precursors and sintering into the optical-ceramic technology. The use of nanocrystal precursors with a narrow distribution in size and high phase homogeneity for obtaining laser ceramic is a critical factor for the success of the technology. For laser ceramic, there are no fundamental technological limitations on large active elements with a composition and dopant concentration that varies over the cross section of the active element. There are also no fundamental limitations on obtaining a laser ceramic based on high-temperature cubic laser materials. This opens up wide possibilities for synthesizing new laser media with improved lasing characteristics. Production costs should be expected to drop when methods of synthesis have been developed that eliminate isostatic pressing of the precursors, as is doubtlessly possible in principle.

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