Methods of synthesis of yttrium-aluminum granate powders for producing transparent ceramics

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Abstract. The work examines the latest research on the synthesis of ceramic powders based on yttrium-aluminum garnet. The advantages and disadvantages of various methods are given. The work highlights the achievements and results achieved by researchers in this field at the moment.

1. Introduction

In the field of laser technology transparent ceramics based on yttrium-aluminum garnet (YAG) have a number of advantages over other transparent materials due to their physicochemical properties. First of all, this is a high operating temperature, with high strength characteristics. Chemical and radiation resistance, mechanical and electrophysical properties make it possible to find its application in various fields of the chemical industry and technology, in measuring instruments operating at high temperatures, in the rocket and space industry. YAG ceramics are characterized by light transmission in a wide range of wavelengths. An important area of its application is laser, LED technology.

When developing and improving methods and technologies for producing ceramics that meet modern requirements, several important aspects can be distinguished: improving the quality of the final product, reducing energy costs, increasing availability, and reducing harmful effects on the environment. Moreover, all technological stages of production must be reproducible.

Obtaining transparent ceramics has its own characteristics. The factors influencing the transparency include: the presence of porosity (closed) > 1 %, the structure of the crystal boundaries, the phase composition, the surface finish of the final product. This, in turn, imposes certain requirements on the starting powders: the starting materials for the manufacture of transparent ceramics must be of high purity, the additives introduced must not violate the monophase system, the additives must be evenly distributed in the system, the linear particle size must not exceed 1 micron with a narrow distribution by size [1]. The requirements for the technology are based on this: the ability to fully control the composition of the starting materials and intermediate products, the ability to influence the final structure of the material - the concept of structure inheritance, the ability to influence the state of the system in a wide range. There are two fundamentally different approaches to the synthesis of ceramic material, incl. YAG: solid-phase synthesis from oxides at high temperatures and pressures, and low-temperature - methods of «soft chemistry». There are intermediate options, such as the «combustion» method, in which heating is required only to initiate the process, and the synthesis occurs due to self-heating of a mixture of precursors (usually nitrates - oxidizing agents) and a reducing agent - an organic component. For solid-phase synthesis, industrial oxide powders are very often used as starting
materials, however, experience shows that the most successful in terms of meeting the requirements for the final product is the use of chemically synthesized powders [2]. There is certainly no universal method for synthesizing ceramic powders. Each of them has its own limits of applicability, it has certain disadvantages and advantages. Some of them involve complex and expensive hardware or require special security measures.

The processes of most methods, in fact, take place in batch reactors that have some degree of imperfection. There are gradients of concentrations of components at the micro level, gradients of temperature and pressure, pH, differences in the deposition rate of metal ions, capture of impurity ions, and the formation of products of incomplete interaction. As a result, the morphology and chemical composition of the particles obtained at the beginning and at the end of the process are different, a broadening of the particle size distribution is observed due to changing conditions during synthesis. There are a large number of methods for the synthesis of YAG powders, which are well covered in the literature. Co-precipitation methods and its various variations due to the simplicity of execution, availability, low temperatures can be attributed to the most common. The essence of the method is the precipitation of sparingly soluble compounds from salt solutions with a reagent - a precipitant. Possible options are solvent replacement, solution cooling. After post-processing (solvent removal, washing, drying, etc.), either a synthesized material ready for sintering or a mixture of precursors in the required ratio and given structure is obtained. The most widespread in the production of YAGs is the precipitation from water-soluble salts (nitrates, chlorides, sulfates) of yttrium and aluminum of their hydroxides, the addition of ammonia, ammonium carbonate, urea or their mixture. Often additives are added at the same time, which also precipitate as oxides / hydroxides or are distributed in the resulting precipitate. The disadvantages include the problems associated with different pH of the precipitation of the components and their different solubility product. Another problem is associated with particle agglomeration, which is typical for a wide range of processes taking place in the aquatic environment. This entails the need for very strict adherence to the conditions of the process. The attention of many researchers is focused on the choice of suitable conditions and on the search for ways to level the negative effect of aqueous electrolytes on the morphology of sediments. Anions, which are part of electrolytes, can be adsorbed on the surface of crystalline deposits or even be incorporated into the structure, influencing the degree of agglomeration of particles. Precipitation in the presence of ammonium sulfate reduces the content of chloride ions and allows one to obtain looser powders with a smaller crystallite size and with more than a hundredfold decrease in the content of chlorine ions (figure 1) [3]:

![Figure 1](image_url)

**Figure 1.** Scanning electron microscopy of disaggregated powders obtained without the use of a dispersant (a) and with the use of (b) [3].

However, as follows from work [4], water, nitrogen and carbon from carbamide and ammonium carbonates are easily removed, and sulfate ions used as a disaggregating agent begin to be removed at
temperatures above 800°C in the form of SO2, and the removal ends at temperatures, comparable to the sintering temperatures (figure 2):

![Figure 2. Mass spectroscopic curves of SO2 gas evolution during the decomposition of the YAG precursor in a stream of air, (v = 50 ml / min; heating rate: 10°C / min).](image)

An original version of the method for producing YAG from a stoichiometric mixture of aluminum, yttrium and niobium salts, which allows one to circumvent some of the above problems, was proposed by the authors of [5]. It is assumed that hexamethylenetetramine with an increase in the temperature of the solution dissociates with the formation of ammonium ions, thereby changing the pH of the medium. The process is carried out in two stages. At the first stage, aluminum hydroxide is precipitated, which has a lower pH of precipitation, then, by increasing the temperature and thereby increasing the pH, the REE hydroxides are precipitated onto the structure of the Al(OH)3 gel (figure 3). Hexamine, possessing a large buffer capacity, is able to stably maintain pH at a given temperature. Knowing the experimentally established dependence pH = f (T) (figure 4), one can clearly control the deposition parameters. As a result, the conditions were selected and nanoscale, weakly agglomerated, monophase Yb:YAG powders were obtained.

![Figure 3. Schematic representation of precursor particles formed during the sequential deposition of aluminum, yttrium and ytterbium hydroxides (a), and a model of the gel structure formed during precipitation with hexamine (b) [5].](image)

One of the most effective ways to increase the non-equilibrium deposition and thereby obtain highly reactive, monophasic powders is spray deposition. The optimal parameters of the sputtering rate and concentration dependences were studied in [6]. The authors, using the obtained powders by the method of gel casting and hot isostatic pressing, produced transparent ceramics with a linear transmittance of up to 80.2 % at 400 nm and 83.1 % at 1064 nm. In addition, the microstructure and laser properties of the transparent ceramics were measured.

A multidimensional study is proposed in the article where the authors, first comparing different synthesis conditions, the effect of surfactants on the morphology and agglomeration of powders, and then the temperature and heating rate during calcination on the structure of ceramics, depending on the
method of obtaining powders [7]. The influence of the molar ratio of ammonium bicarbonate to metal ions (R) on the structure of powders and on the structure of sintered samples is clearly demonstrated in the study (figures 5-6) [8]:

![Figure 4](image1.png)

**Figure 4.** Dependences of pH on temperature for aqueous solutions of hexamine [Hex] and ammonium sulfate with hexamine [Hex + (NH₄)₂SO₄] [5].

![Figure 5](image2.png)

**Figure 5.** SEM-image of Nd:YAG powders calcined at 1100 °C with different R values: (a) R = 3.0; (b) R = 3.2; (c) R = 3.4; (d) R = 3.6; (e) R = 3.8; (f) R = 4.0 [8].

The boundary between some methods of obtaining powders is rather arbitrary. Depending on the reaction conditions, the precipitation of many hydroxides can pass through the stage of sol- and gelation [9]. This phenomenon is widely used in the technology of YAG production. Using the sol-gel methods, depending on the subsequent processing of the sol, films, fibers, powders can be obtained. The formation of a structured system is an advantage of the method, it allows to implement the concept of structure inheritance by the final material. Preparation of crystalline materials with a garnet structure Y₃Al₅O₁₂ (YAG), Y₃Sc₂Al₁Ga₁O₁₂ (YSAGG-3212), Y₃Sc₁Al₃Ga₁O₁₂ (YSAGG-3131), Y₃Sc₂Al₃O₁₂ (YSAG), Y₃Al₁Ga₂O₁₂ (YAGGa) [10].

The most widely used types of the method: citrate [11], glycolate [12], hydroxide [9], alkoxide [13] and some others. Gels containing organic combustible substances can either be subjected to heat treatment in order to remove ("burn out") the organic component, or, having inorganic precursors in
the form of nitrates, ignite. In the latter case, the exothermic combustion reaction of the mixture leads to the synthesis of the required product. The method is called the “combustion” method [14]. The peculiarities of the combustion method without the formation of gels are considered in [15], where the authors obtained YAG doped with cerium. In [16], to obtain YAG luminophores of the same composition, aluminum was used as a reducing agent, and oxygen evolved when heating sodium perchlorate, which is part of the reaction mixture, served as an oxidizing agent.

Figure 6. SEM-image of Nd: YAG ceramics sintered at 1700 °C with different R values: (a) R = 3.0; (b) R = 3.2; (c) R = 3.4; (d) R = 3.6; (e) R = 3.8; (f) R = 4.0 [8].

The temperatures developed during the thermal reaction reached 3500 °C, which required the use of special equipment, shown in figure 7.

Figure 7. Schematic diagram of an experimental setup for preparing samples by the combustion method.

Among the methods used and developed for the production of optically transparent ceramics from YAG, we would like to highlight the modification of the sol-gel methods using REE and aluminum alkoxides as precursors. Metal alkoxides as promising agents for sol-gel technology have been known
for a long time [17]. However, in the literature, the methodology for the synthesis of yttrium-aluminum garnets with their help is insufficiently illuminated in our opinion. Alkoxides are highly reactive substances. Their true composition does not always correspond to the stoichiometric one [18]. This is caused by the formation of oxo-alkoxo compounds under the influence of a number of factors: during hydrolysis, initiated by traces of moisture, oxidation, with the formation of peroxides, giving rise to radical side processes, thermolysis, decomposition with the elimination of ethers [19]. Condensation with the elimination of ethers appears to be one of the most important pathways for the spontaneous decomposition of alkoxides. In the opinion of most authors, the formation of hydroxides occurs through the oxo-alkoxide stage as a kinetically and thermodynamically favorable path. Just as in the aging process of hydroxide sols and gels, caused by the formation of M-O-M bonds with the elimination of water, here the formation of such bridges occurs with partial esterification of alkoxides. It is important to emphasize that from an uncontrolled side process, the formation of oxo compounds, can be converted into a controlled reaction for obtaining hydroxides with a given spatial structure. Alkoxides tend to form cluster structures; the nuclearity of various homoleptic complexes varies from mononuclear to decanuclear [20]. It has been experimentally proven that oxoalkoxides exist in the form of polyhedral molecular structures. Examples of some of them are presented in figures 8-9.

Figure 8. An example of the structure of REE isopropoxides [18].

Figure 9. The structure of aluminum ethoxide [18].

Most authors believe that the mechanism and kinetics of the sol-gel formation of their alkoxides have not been sufficiently studied. But nevertheless, some factors are identified that determine the nature of the reaction, the composition and morphology of the final product. These include: temperature, concentration, viscosity of the medium, the nature and volume of the ligands, the pH of the medium, the amount of water or other hydrolyzing agent. It is believed that the hydrolysis process is highly non-equilibrium. The speed depends on many parameters and is limited by the first stages. By selecting the parameters of the process, it is possible to obtain gels with a structure close to the structure of the final material, in fact, to “design” the structure of the future material. This practice has been successfully applied for the synthesis of barium titanates of various crystallographic structures from binuclear alkoxo complexes [19]. Due to the fact that the synthesis is carried out in organic solvents, the aggregation of powders is several times slower than in an aqueous medium. The
aggregation stability of sols is also much higher due to the low electrolyte content. Aggregation can be further reduced by using vacuum to remove the solvent. The significant advantages of the sol-gel technology based on alkoxides include the possibility of deep purification of the starting compounds. Mono- and bimetallic oxides are obtained in the form of amorphous preparations, which consist of nanosized particles with high reactivity. This allows ceramics to be sintered at lower temperatures than alternative technologies. In the synthesis of complex oxides, the use of alkoxide solutions makes it possible to overcome the main difficulty of other methods - the achievement of homogenization of atoms of various metals at the molecular level. Subsequent hydrolysis and heat treatment of such samples results in submicron particles. The introduction of additives is possible immediately before or during the hydrolysis process. This achieves a very uniform distribution in the resulting powders. The alkoxide sol-gel method is widely used to obtain various materials: films, fibers, glasses, many types of ceramics, including optically transparent ones. However, the relative share of publications devoted to this method for obtaining ceramics from YAG is small. Moreover, the method makes it possible to obtain powders for YAG - high quality ceramics. Its further development seems to be very promising.

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