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Production of Nanodisperse Particles of Doped Yttrium–Aluminum Garnet by a Sol-Gel Process

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Abstract—Method for synthesis of nanodisperse yttrium–aluminum garnet powders activated with cerium and silicon ions was developed. The method is based on a combination of sol-gel synthesis and coprecipitation of hydroxides of the corresponding metals. The process modes were optimized and the structural, physicochemical, and spectral-luminescent characteristics of the samples obtained were studied.

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Yttrium–aluminum garnets (YAGs) doped with ions of rare-earth elements (REEs), which have a stable crystal structure, increased radiation hardness and thermal stability, and high heat conductivity, combined with low electrical conductivity, and high resistance to deformation and oxidation, find exceedingly wide use (primarily in optics and laser technology) owing to their intense luminescent properties [1].

The classical way to synthesize single crystals, Czochralski method, requires very high temperatures and intricate equipment [2, 3], and, therefore, modern optical materials science prefers to use a polycrystalline ceramic, including that based on YAG, as a working material. The best samples of a ceramic of this kind surpass single crystals in both strength and optical properties [4]. As starting materials serve nano (ultra) disperse YAG powders activated with REEs, whose synthesis attracts a particular attention. The solid-phase synthesis of YAG powders from oxides require high temperatures (>1600°C) [5, 6]. The techniques used to synthesize YAG powders include hydrothermal [7], solvothermal [8], combustion [9, 10], coprecipitation [11, 12], and sol-gel [13, 14] methods, as well as sonochemistry and microwave radiation [15].

All these techniques have certain disadvantages, and, therefore, modification of the existing methods for synthesis of garnets and development of new methods to control the purity of the product and particle size and diminish the material processing temperature to the maximum possible extent are of fundamental importance.

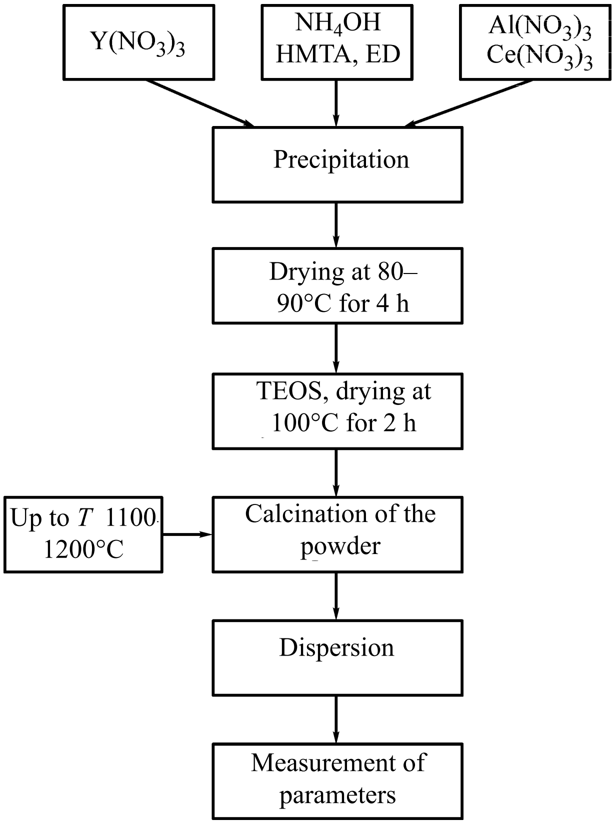
In this communication, we suggest a new approach to synthesis of YAGs, based on a combination of coprecipitation followed by a sol-gel process. As object of study is chosen a cerium-doped YAG, widely used as an active component in white light-emitting diodes (LEDs) [16–19].

EXPERIMENTAL

Synthesis of YAG powders by coprecipitation of yttrium and aluminum hydroxides with ammonia (see scheme) includes preparation of a mixture of yttrium and aluminum nitrates in relative amounts (in terms of oxides) corresponding to the stoichiometric formula of yttrium–aluminum garnet $Y_3Al_5O_{12}$ and addition of a 20% ammonia (NH_4OH) solution and a solution of hexamethylenetetramine (HMTA) or ethylenediamine (EDA) under vigorous agitation.

To obtain a doped powder, we introduced activator ions (cerium, 1% relative to the mass of YAG) into the stock in the form of a nitrate salt. To intensify the agitation and obtain a stable homogeneous transparent sol, we simultaneously used the mechanical (stirrer) and ultrasonic agitation. The resulting sol in an open Teflon vessel was placed in a drying box for 4 h (*T* = 80°C), where it was converted into a gel and further into a solid powder. After that the powder was ground in a mortar or attritor and tetraethoxysilane (TEOS) was added (30 ml of TEOS per 35 g of dry stock). After a second thermal treatment in a drying box at a temperature of 100°C (2 h), a sample was heated to 450°C for 2 h and calcined at 1000°C in air (in argon) in a muffle furnace for 3–4 h.

Scheme of synthesis of a YAG powder by coprecipitation in ammonia



The main concept of the study consists in that TEOS is introduced into the system. Under conditions of a limited amount of water present in the precursor of the YAG powder, its hydrolytic polycondensation under the action of ammonia leads to formation of linear (cyclic) oligosiloxanes [20] uniformly distributed over the mass of the sample. In the process, the removal of water apparently precludes agglomeration of garnet particles. As shown by experiments, 30 ml of TEOS is the optimal amount for treatment of 35 g of the YAG powder. A smaller amount is insufficient or full wetting of particles, and a greater amount evaporates (decomposes) in thermal treatment. The subsequent heating of the YAG precursor powder to 1000°C leads, after the resulting alcohol evaporates at 100°C, and the excess amount of TEOS, at 200°C, to thermal decomposition of oligosiloxanes to give hydrocarbon derivatives that create a weakly reductive medium and improve the

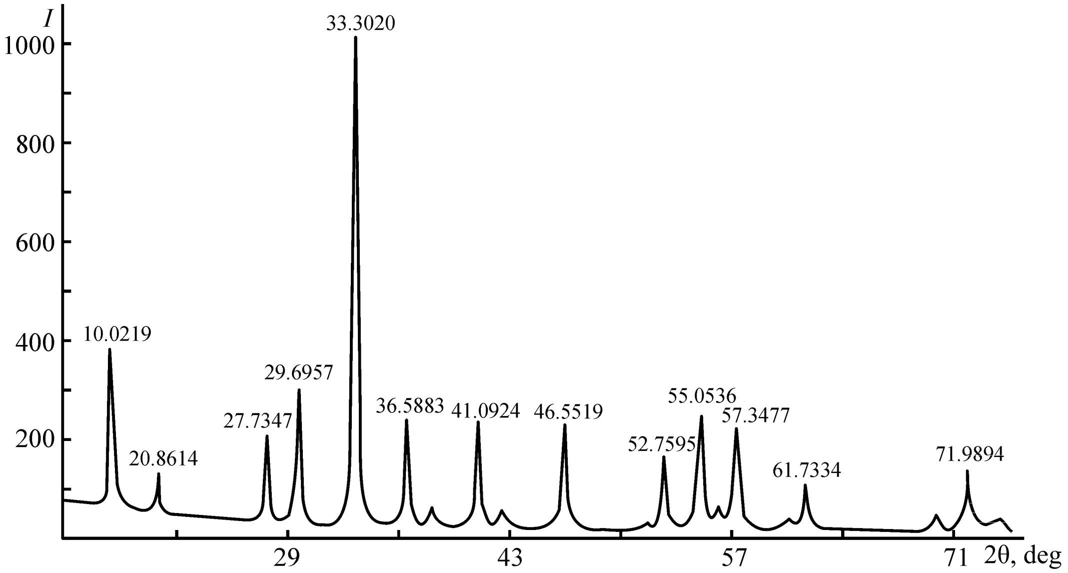


Fig. 1. X-ray diffraction pattern of YAG obtained by precipitation in an ammonia solution. (*I*) Intensity and (2θ) Bragg angle.

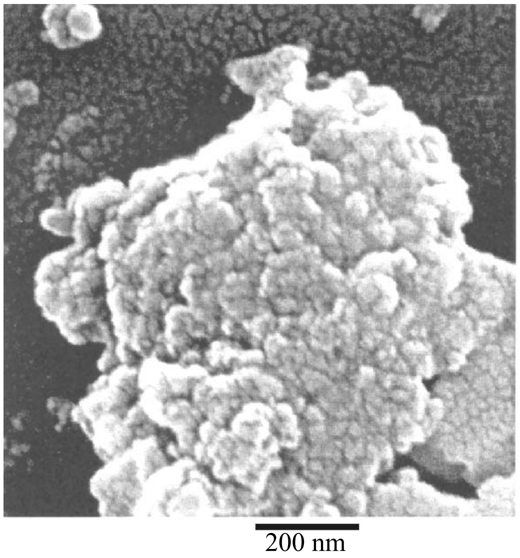


Fig. 2. SEM image of a YAG powder produced by coprecipitation.

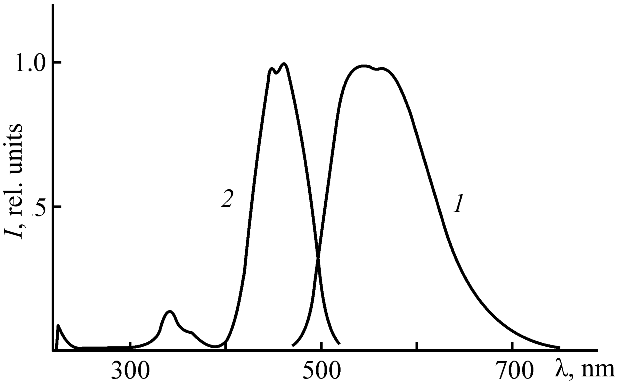


Fig. 3. Normalized spectra of (*1*) luminescence and (*2*) luminescence excitation for a phosphor based on YAG : Ce^{3+}. (*I*) Normalized intensity and (λ) wavelength.

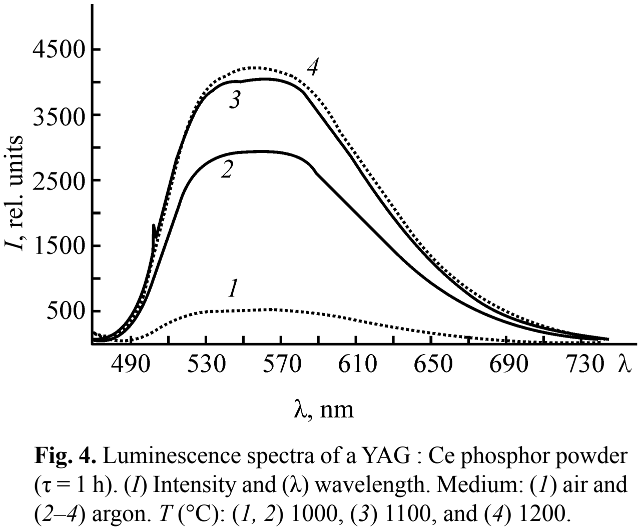


Fig. 4. Luminescence spectra of a YAG : Ce phosphor powder (τ = 1 h). (*I*) Intensity and (λ) wavelength. Medium: (*1*) air and (*2–4*) argon. *T* (°C): (*1, 2*) 1000, (*3*) 1100, and (*4*) 1200.

luminescent characteristics of the YAG–Ce system.

An X-ray diffraction pattern of the YAG powder is shown in Fig. 1. According to the XPA data, the main phase of the product yielded by precipitation in ammonia and HMTA, followed by thermal treatment at 1000–1300°C, is a garnet of composition $Y_3Al_5O_{12}$, whereas the precipitate produced by interaction with EDA contains free aluminum and yttrium oxides. A probable reason for this difference between the powder compositions is that HMTA is a milder precipitating agent than EDA. The electron micrograph in Fig. 2 demonstrates that rather dense associates of nearly spherical nanosize particles are formed.

Figure 3 shows luminescence excitation and luminescence spectra of the resulting activated YAG powder. It can be seen that, when excited with blue light (λ_{ex} = 450 nm), the YAG : Ce^{3+} sample luminesces at 470–700 nm (i.e., in the visible spectral range with a shift to a “warmer” region).

To examine the effect of various types of thermal treatment of phosphor powders in gaseous media on the luminescence intensity, we performed experiments on calcination of the synthesized YAG materials in air and in argon at temperatures of 1000–1200°C. As follows from Fig. 4, treatment of the YAG : Ce powder in argon leads to an approximately 8-fold rise in the luminescence intensity, presumably because of an increase in the fraction of triply charged cerium responsible for the yellow-green luminescence in the surface layer of garnet particles.

The luminescent powders we obtained were used to design a lamp based on blue LEDs, which can produce scattered white light [21].

CONCLUSIONS

(1) The method for production of nanodisperse powders in the Y_2O_3–Al_2O_3 : Ce system from the corresponding nitrate salts, based on a combination of coprecipitation and sol-gel synthesis, makes it possible to synthesize yttrium–aluminum garnets without admixture of other phases.

(2) The material obtained shows a high-intensity luminescence and can be used to convert short-wavelength light from blue LEDs into white light with a pink hue.

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