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Preparation, spectroscopy and morphology of Nd:YAG nanostructures*

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The neodymium-doped yttrium aluminum garnet (Nd:YAG) nanocrystalline powders were prepared by sol-gel method. The synthesis of semitransparent polycrystalline ceramics is described. Their structure and morphology were studied by means of XRD and TEM methods. It was found that with increasing thermal heating the sizes of Nd:YAG grains increase. Optical properties of Nd^{3+}:YAG nanocrystalline powders and ceramics are reported. The evident influence of the grain size on the luminescence of Nd^{3+} ions has been observed.

Key words*: YAG, nanocrystalline ceramics, Nd^{3+} emission*

1. Introduction

Since discovery of the stimulated optical radiation in Nd^{3+}:YAG [1] this crystal found the most common application in quantum electronics. In recent years, the rare-earth ions-doped yttrium-aluminum garnet (YAG) single crystals have been the most widely used solid-state laser materials [2]. In the practical application as luminescence activator Nd^{3+} plays a more important role than do Ho^{3+}, Tm^{3+} and Er^{3+} ions. The Ce^{3+}, Tb^{3+} and Eu^{3+}-doped YAG particles are also the subject of intense studies in view of their stability at the conditions of high irradiance as efficient host material of full-color phosphors [3, 4]. Crystal structure of $Y_3Al_5O_{12}$ is of characteristic cubic symmetry with lattice parameter a = 12.004 Å. The first attempts to construct the solid-state laser based on polycrystalline ceramics have been reported by de With et al. [5], Mudler et al. [6] and Sekita et al. [7]. The first reports on Nd^{3+}-doped transparent ceramics fabricated by hydroxide co-precipitation process, solid-state reaction among oxides

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powders and vacuum sintering, adequate for optical applications and able to emit a laser beam were notified by Greskovich et al. [8], Vrolijk et al. [9] and Ikesue et al. [10–12]. This technique generally requires heat treatment at high temperatures above 1600 °C and in a special case of mechanical mixing [13]. The ceramics were composed of the grains of few tens microns. The highly transparent crystalline ceramics obtained by isostatically pressed method [8, 12] were characterized by excellent optical properties sufficient for laser operation. In recent years, there have been reported new low-temperature synthesis methods of fabrication of nanosized YAG crystallites by different wet chemical processes, i.e., a nitrate process [14], homogeneous precipitation [15–17] and alkoxide-acetate process [18]. In the case of homogeneous precipitation and alkoxide method (sol-gel method) there was reported a direct crystallization at YAG below 1000 °C [14]. In this work, we present the results of preparation and characterization of Nd^{3+}-doped $Y_3Al_5O_{12}$ obtained by a modified sol-gel technology similar to that developed by Vaqueiro and Lopez-Quintela [15].

2. Experimental

Stoichiometric amounts of yttrium chloride (99.99%), aluminum nitrates (99%) were dissolved in aqueous citric acid solution to give a molar ratio appropriately of 3:5:16. Neodymium chloride (99.99%) was added in the precursor solution to give a Y:Nd atomic ratio of 100:5 and ultrasonically stirred for 2h at about 80 °C. The obtained solution was gelated at 80 °C for several hours and dried at 110 °C during the period of 3 days. Samples of the crushed gel were heat-treated at different temperatures in the air in an electric oven. In order to form crystalline Nd:YAG powders, the obtained gels were heated at 800 °C (sample A) and 1000 °C (sample B) for 16 h. Then, ceramic disks were fabricated from the sample A which was pressed at about 200 MPa in the air and in vacuum and sintered at 750 °C (samples C and D, respectively) and at 1400 °C (sample E) in the air for 16 h.

The microstructure of samples prepared was evaluated by transmission spectroscopy (TEM – Philips CM20 SuperTwin Microscopy operating at 200 kV and providing 0.25 nm resolution) and X-ray diffraction (XRD – Stoe Powder Sensitive Detector; filtered $CuK\alpha_1$ radiation). Absorption spectra were measured at room temperature with a Cary 5 spectrophotometer. Emission spectra were measured at room temperature using Jobin-Yvon TRW 1000 spectrophotometer and a photomultiplier (Hamamatsu R406). All recorded spectra were corrected according to its characteristics. Emission lifetimes were measured by means of Tektronics TDS 380 oscilloscope. As excitation source we used the 532 nm line of doubled Nd:YAG laser.

3. Results and discussion

All the samples studied were light-blue. The structural analysis of samples as a function of the heating temperature is shown in Fig. 1. A lack of broad peaks indicates the high crystallization and ordering state of crystallites. Sharp peaks in the all recorded XRD patterns could be ascribed to cubic $Y_3Al_5O_{12}$ [19] and are the narrowest for the sample E (the largest crystallites). The average sizes of nanocrystallites were determined from the broadening of diffraction lines of X-ray patterns according to Scherrer's formula [20] and were estimated to be 25 nm for the samples A, C, D, and 98 nm and above 150 nm for the samples B and E, respectively. The evaluated values are confirmed also with transmission electron micrograph (TEM) presented below.

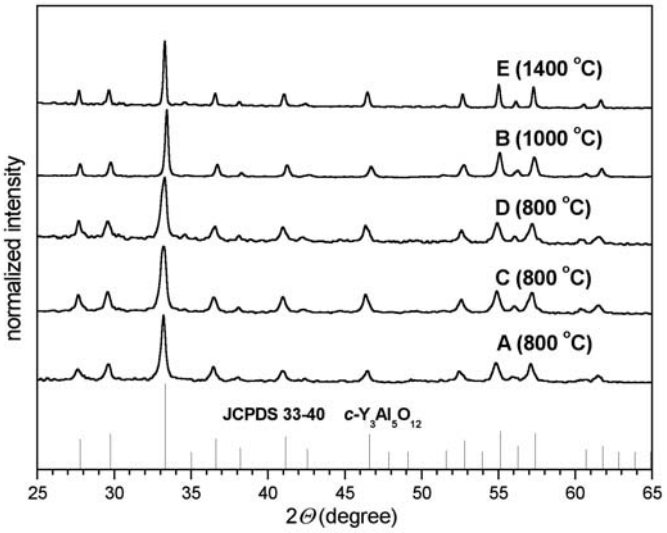

Fig. 1. XRD patterns of Nd:YAG heated at different temperatures: A – powder 800 °C, B – powder 1000 °C, C – pellet 750 °C, D – pellet 750 °C and E – pellet 1400 °C

The microstructures of Nd:YAG nanocrystallites are shown in Fig. 2. In TEM images of powders (Fig. 2a) dispersed grains of $Y_3Al_5O_{12}:Nd^{3+}$ (sample A) and the aggregates composed of this grains (Fig. 2b) for powder heat-treated at the higher temperature (sample B) are visible. The TEM images of powdered pellets (samples C and E, respectively, Figs. 2c, d) indicated that with increasing temperature of thermal treatment the size of grains increased by gradual aggregation and bonding of the smaller grains. One can note an increase of crystallite size with heating temperature from about 25 nm for sample A to 138 nm for sample E. These results are in agreement to the XRD data.

The absorption spectra of Nd:YAG nanocrystallites were recorded at room temperature. A comparison of the absorption spectra for the specimen pressed in air (sample C) and in vacuum (sample D) is shown in Fig. 3. The respective absorption transitions were determined and marked in the figure. One can note that for the same concentration of Nd^{3+} ions (1%) we have observed more distinct absorption bands for sample D compared to the sample C. High background in the blue region of spectra follows from rather poor low transparency of both samples.

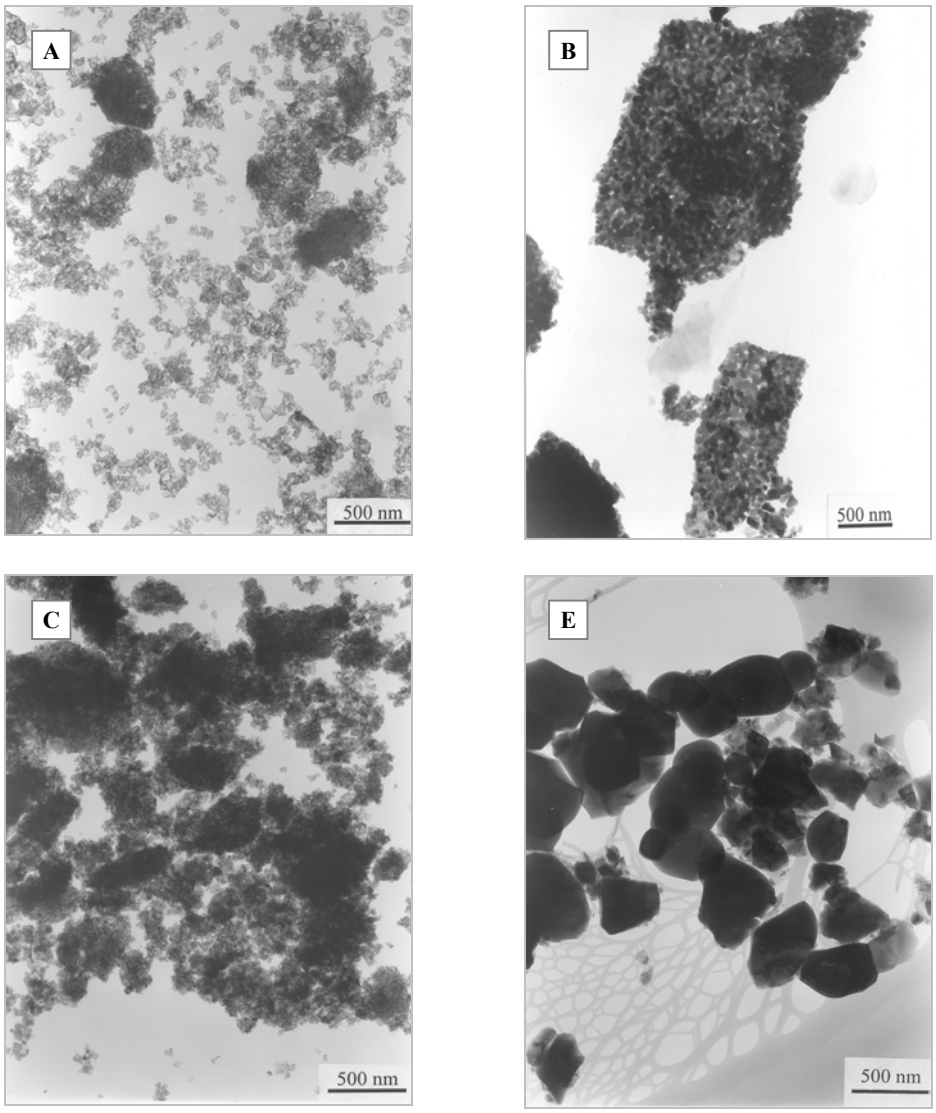

Fig. 2. TEM images of Nd:YAG nanocrystallites: A – powder 800 °C, B – powder 1000 °C C – pellet 750 °C pressed in air and E – pellet 1400 °C

The emission spectra of Nd^{3+}:YAG nanocrystallites measured at room temperature are shown in Fig. 4a. The spectra consist of two characteristic bands attributed to the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ (810–910 nm) and $^4F_{3/2} \rightarrow {}^4I_{11/2}$ (1040–1070 nm) transitions. The positions of all emission lines are almost identical to those reported for Nd:YAG crystal.

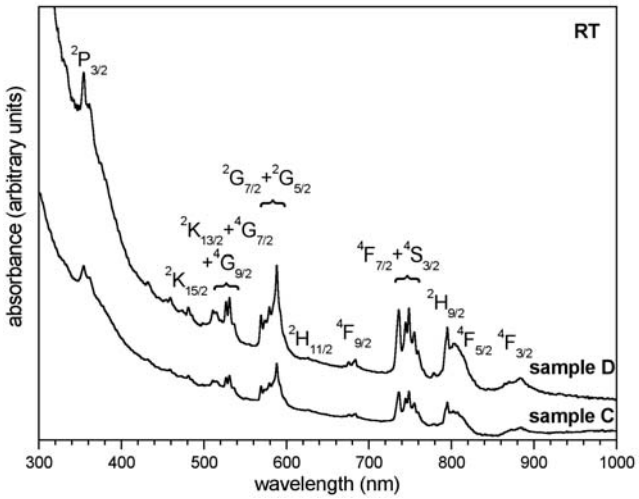

Fig. 3. Absorption spectra of Nd:YAG nanocrystalline ceramics obtained at two different temperatures of thermal treatment – the sample C (pellet 750 °C pressed at air), and the sample D (pellet 750 °C pressed in vacuum)

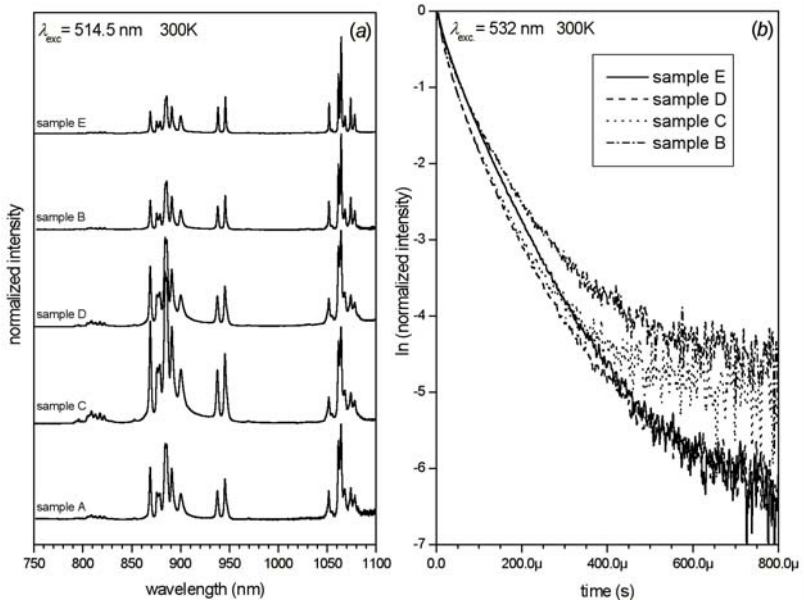

Fig. 4. Emission spectra of Nd:YAG nanocrystalline ceramics prepared at different temperatures of thermal treatment (a) and decay curves of Nd:YAG nanocrystallites emission at 884 nm measured at 300K after 532 nm pulse excitation (b)

It is interesting to note that in the range of 800–830 nm there was observed the band attributed to the $^4F_{5/2} \rightarrow {}^4I_{9/2}$ transition. It is extremely intense for the samples heated at lower temperature for which the crystallites sizes are the smallest. It was the strongest for the pellet pressed in air. With increasing crystallite sizes this band became much weaker (see B and E). Moreover, it is interesting to note that with increasing sintering temperature the intensity of the laser transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ increases compared to the second $^4F_{3/2} \rightarrow {}^4I_{9/2}$ band. This increase is most probably due to the increase of the nanocrystallite size. However, its nature needs further investigations. A comparison of the emission bands of the two pellets, the first pressed in air (C) and the second pressed in vacuum (D) points to strong enhancement of the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ band intensity compared to the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ band.

Table. The decay times observed after excitation by 532 nm line of a pulse line Nd:YAG laser measured at 300 K (decay times were approximated to the shortest and the longest component of each decay curve)

Sample	Size of grains/nm	τ_{short}/μs	τ_{long}/μs
C	25	20	120
D	25	20	137
B	98	20	152
E	138	30	128

We measured the dependence of the lifetimes of band attributed to the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition on the size of Nd:YAG grains. The examples of emission decays measured at 884 nm are shown in Fig. 4b. The observed decay curves are distinctively non-exponential and are typical of heavily Nd-doped samples [22]. Such non-exponential curves could be approximated by many decays. Therefore, it is more reliable to find the shortest and the longest component. In our opinion, the first component is due to the concentration quenching of Nd^{3+} ions, and second to the isolated Nd^{3+} ion. Both the decay time components were evaluated from the decay profiles and are shown in the table. One can note that only the longest component evaluated for the sample B increases compared to the samples C and D to be 101 μs, 138 μs and 152 μs, respectively. We can explain this effect by removing OH groups from the closest surrounding of Nd^{3+} ions. The longest component of decay time estimated for the sample E is shorten more than those for the samples D and B. In our opinion, this fact is due to the aggregation process associated with grain increase.

4. Conclusions

The purpose of present paper was to report the modified synthesis of Nd:YAG nanocrystallites obtained by sol-gel method. Their morphology was investigated by XRD and TEM methods. It was found that with increasing temperature of thermal

treatment the size of Nd:YAG grains increased. The semitransparent ceramics composed from the Nd:YAG grains were prepared. Their absorption and emission properties were investigated. It was found that with increasing temperature of thermal treatment the intensity of $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition increased compared as to the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ band. It was shown that the decay time of the luminescence was dependent on the size of the crystallites grains. Moreover, we have observed the emission originating from the $^4F_{5/2}$ state in small-size grains.

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