

## STUDIES ON SOL-GEL PROCESSES ACCOMPANYING FORMATION OF THE YTTRIUM ALUMINUM GARNET NANOCRYSTALS

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The sol-gel processes of YAG and YAG doped Nd are presented. The mechanism of YAG powders formation by sol-gel method is described. The gel is formed by reaction of inorganic salts or oxides Y, Al, Nd elements with acetic acid and ethylene glycol. Conditions of sol-gel processes in the range of temperature treatment from 100°C to 1000°C and mechanism of reactions are investigated using DTA, X-ray diffraction and infrared spectroscopic methods. Size, shape, and morphology of the surface of the YAG powders are characterized by scanning electron microscope. Finally one phase of YAG and yttrium substituted by neodymium up to 28% at. are found. At higher concentration of Nd (up to 100% at.) two phases of garnet and perovskite type are detected.

### 1. INTRODUCTION

The materials applied in laser, or more generally electrooptical, devices must satisfy very high requirements: high purity, homogeneity and phase uniformity. The wet chemical methods [1] are superior to physical methods and reactions in solid phase, because in water solution diffusion proceeds easily and homogeneity at the molecular level is achievable effortlessly. There are three main wet methods used for synthesis of optical materials: cryochemical, coprecipitation, and sol-gel. Each of them allows obtaining homogenous and amorphous or nanocrystalline materials, and each of them can be disadvantageous. The cryochemical methods require expensive equipment, the coprecipitation methods are very sensitive to pH variations, and the sol-gel method is time consuming. The latter has, however, important advantages over the first two [2-3]. The reasons for the particular value of and interest in sol-gel synthesis are given below.

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- The temperature required for all stages are low, frequently close to room temperature. Thus thermal degradation of both the material itself and any entrapped species is minimized, and high purity and stoichiometry can be achieved.
- The low temperature of sol-gel processes is generally below the crystallization temperature for oxide materials, and this allows the production of unusual amorphous and nanocrystalline materials.
- Since precursors involving different metals are frequently miscible, homogenous controlled doping is easy to achieve.
- By using organometallic precursors containing polymerizable organic ligands, materials may be produced which contain both inorganic and organic polymer networks.
- The chemical conditions are mild. In this way pH sensitive organic and biological species may be entrapped and still retain their functions.
- Since liquid precursors are used it is possible to cast ceramic materials in a range of complex shapes and to produce thin films or fibres as monoliths, without the need for machining or melting.

The sol-gel method is well established: the first scientific papers based on the method were published at the beginning of the XX century [3]. Recently, thanks to discovery of many new material characterization methods, the properties of the sol-gel method was fully appreciated and so formed materials are often called "advanced new-generation materials" [4-6]. Therefore, the sol-gel methods become useful to produce materials for optoelectronic and optocommunication (photonic). Nanocrystalline oxide powders doped with rare-earth ions exhibit a strong luminescence. They may be used to produce laser ceramics and photonic wires [7-9]. In particular, the yttrium aluminum garnet (YAG) doped with the rare-earth ions is very valuable laser optical material [10-13]. Formation of this material in the monocrystalline form is an expensive and time-consuming process. Thus, the idea to synthesize the YAG nanopowders to be next sintered has arisen [14-19].

The powder precursors of the yttrium aluminum garnet can be obtained at three main ways. The first base on a reaction in the solid phase and proceeds through sintering of the size-reduced and well-mixed yttrium oxide and aluminum oxide powders in 1750°C [14-16]. The other two methods are wet chemical methods that are based either on coprecipitation or sol-gel formation. In the coprecipitation method, the grains of the YAG structure are obtained by dissolution of water-soluble salts, which next are alkalized for the pH enables entire transformation of the metal ions to yttrium and aluminum hydroxides [17-19]. After removing of the anions adsorbed at the surface of deposit, it was calcinated at 1000°C -1200°C. The synthesis of the nanopowders by the sol-gel method bases on formation of a water colloid suspension (sol) in the course of hydrolysis of metal compounds to hydroxides. The sols transform next into sticky gels, and after drying at 120°C, into solid xerogels. The

polycrystalline YAG precursor powders are formed as a result of thermal treatment - calcination at 1000°C [20-22].

Precursors of YAG nanocrystals can be obtained by two routes using its metal compounds: alkoxides or inorganic salts and oxides. Originally the alkoxides way was applied [20]. But preparation of YAG using metal alkoxides is very expensive, sophisticated and time-consuming manner. The second way based on inorganic salts and metal oxides is faster, cheaper and less complicated. It requires additionally using complexing agents: citric acid [21-23], glycol ethylene [24-25] or ethylenediamine-tetraacetic acid (EDTA) [26-27].

The mechanisms of the sol formation from the inorganic salts, which are different from those accompanying alcoholate pathway, were not explained sufficiently. Moreover, the process of the thermal treatment of the xerogel was not discussed enough.

The aim of the present paper is to adopt the glycolate method described by Veith [24] to produce large amounts of the YAG precursor, both pure and highly neodymium doped, as well as to study on the synthesis mechanism.

## 2. SYNTHESIS

The following substances were used: yttrium oxide  $Y_2O_3$  and neodymium oxide  $Nd_2O_3$  4N purity, aluminum nitrate nonahydrate  $Al(NO_3)_3 \cdot 9 H_2O$ , acetic acid  $CH_3COOH$ , nitric acid  $HNO_3$  65%, ethylene glycol - all analytical grade and deionized water.

In our procedure  $Y_2O_3$  (15.691 g, 0.06949 mol) was dissolved in 600 ml of 0,4 mol/l solution of the acetic acid. The solution was agitated for 10 hours at temperature of 55°C – 60°C. During the course of the reaction, the pH was monitored and, when needed to preserve pH in the range of 4.5-5.0, the concentrated acetic acid was added to protect from metal oxide flocculation. Next, 86.89 g (0.2316 mol) of  $Al(NO_3)_3 \cdot 9 H_2O$  was dissolved in 250 ml of distilled water and the so obtained solution was added to the first one, and next agitated for the next 2 hours at the same temperature. At the end, 26.4 ml-0.471 mole of ethylene glycol was added. During concentration by slow evaporation at 60°C – 70°C, the agitated solution containing Y, Al, acetate, nitrate, and glycol, transformed into a white-transparent gel, which after drying at 100°C – 120°C changed its color into brownish. The dried xerogel powder was size-reduced within two hours at 800°C in the air atmosphere. Because, organic compounds containing gels are flammable, the slow temperature increase (ca. 2°/min) was applied, especially in the temperature range of 150°C – 400°C. After, the additional size-reduction, the powders were six hours calcinated at 800°C – 1600°C in the air atmosphere.

To obtain the garnet doped with Nd, together with yttrium oxide the neodymium oxide was introduced into the reaction solution. Table 1. contains quantities of metal oxides necessary for obtaining 100 g of the precursors containing different Nd<sub>2</sub>O<sub>3</sub> concentrations.

**Table 1.** Amounts of Y, Nd, and Al compounds used for obtaining 100 g YAG nanopowders doped with Nd.

**Tabela 1.** Ilości Y, Nd i Al użyte do otrzymania 100 g nanoproszków YAG domieszkowanych neodymem.

Nd concentration (mol %)	Nd <sub>2</sub> O <sub>3</sub> mass (g)	Y <sub>2</sub> O <sub>3</sub> mass (g)	Al.(NO <sub>3</sub> ) <sub>3</sub> · 9 H <sub>2</sub> O mass (g)
1	0.8503	56.4977	315.97
2	1.7006	55.9106	315.97
4	3.4012	54.7815	315.97
6	5.1018	53.1078	315.97
8	6.8024	51.9779	315.97
10	8.5030	50.8480	315.97
12,5	10.6300	49.4354	315.97
15	12.7545	48.5081	315.97

### 3. MEASUREMENTS

Thermal analysis of the YAG xerogel destruction at the temperature range 20°C – 1000°C and temperature increase of 2°C/min, was performed by using the STA 409 derivatograph produced by NETZSCH.

The structural changes during the thermal treatment of the xerogel powders were monitored by using the X-ray diffraction method carried out with the Siemens D-500 diffractometer equipped with a semiconducting silicon detector doped with the lithium ions. The measurements were performed by using the 0.05° step-scan measurements within the 2θ angle range of 15° – 65°, acquisition time of 4 s, and Cu K<sub>α</sub> 1.548 Å wavelength.

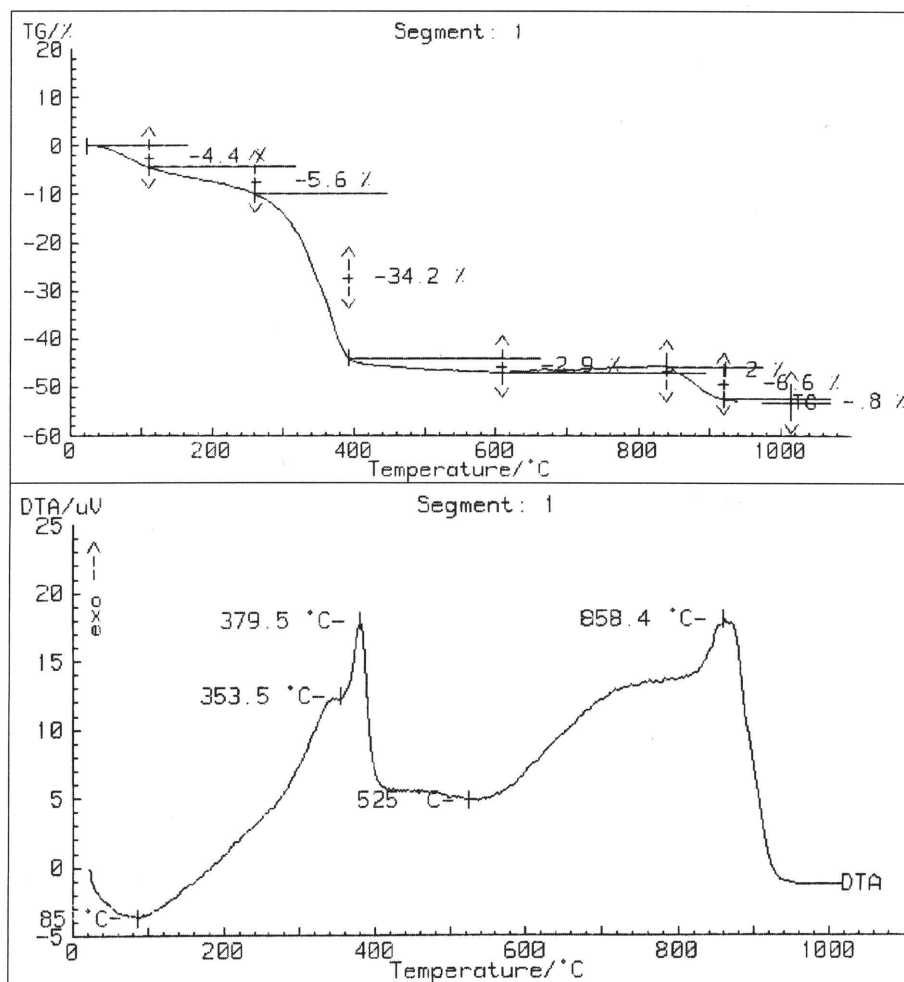
Size, shape, and morphology of the surface of the YAG powders at different stages of the thermal treatment were followed based on scanning electron microscope DSM-950 (produced by OPTON) images in the secondary electrons beam. The size of the powder particles and their statistical distribution were evaluated based on photographs analyzed by TV image analyzer (produced by Clemex, Canada).

The mid infrared spectra (4000 cm<sup>-1</sup>– 400 cm<sup>-1</sup>) were recorded by using the Perkin-Elmer System 2000 FTIR spectrometer with 4 cm<sup>-1</sup> resolution. The samples

were measured in form of the KBr pellets made by mixing 2 mg of the YAG powder with the 800 mg of KBr and compressed under ca. 250 atm. The spectra were recorded against an analogous pellet made from pure KBr.

#### 4. RESULTS

The graph representing thermal analysis of the YAG xerogel pyrolysis in the temperature range 25°C-1000°C is presented in Fig. 1. The upper curve (TGA) reflects

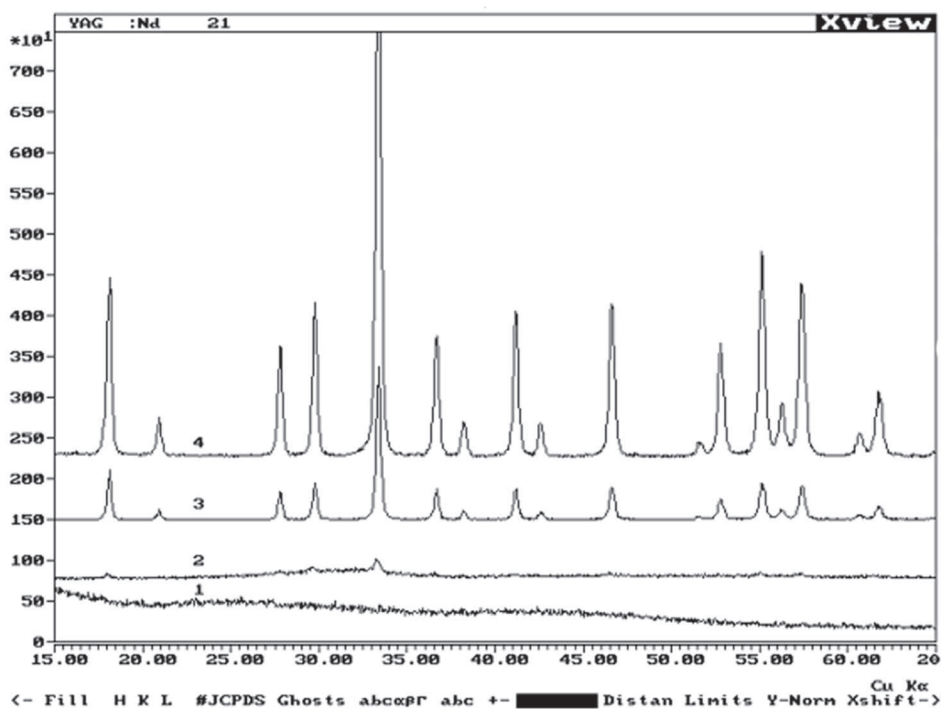


**Fig. 1.** TGA and DTA curves of YAG xerogels, temperature increase of 2°C/min.

**Rys.1.** Krzywe TGA i DTA wykonane dla kserożelu YAG, wzrost temperatury 2°C/min.

mass decrease with increase of temperature, whereas the lower curve (DTA) displays characteristic temperature points at which processes accompanying to pyrolysis proceed. The decrease of the xerogel mass, which at the end reaches 53.25%, proceeds in several stages, which go with heat effects (Fig. 1). The first mass attenuation of 4.4% is connected with an endothermic process, whereas the other three with exothermic processes. The largest heat effect at temperature equal to 379°C comes with the largest mass attenuation of 34.2%. In the temperature range 600°C – 840°C one can observe a slight mass increase, a matter of 1.2%, and a slightly exothermic reaction. The second high heat effect reaches its maximum at 858°C, however, the accompanying mass decrease is lower than that at 379°C and is equal to 6.6%.

The dependence of the X-ray lines of the YAG powders on the  $2\theta$  diffraction angle is depicted in Fig. 2, where the spectra 1-3 refer to pure YAG and the spectrum 4 refers to YAG doped with 4 mol % of  $\text{Nd}_2\text{O}_3$  thermal treated in different temperatures.

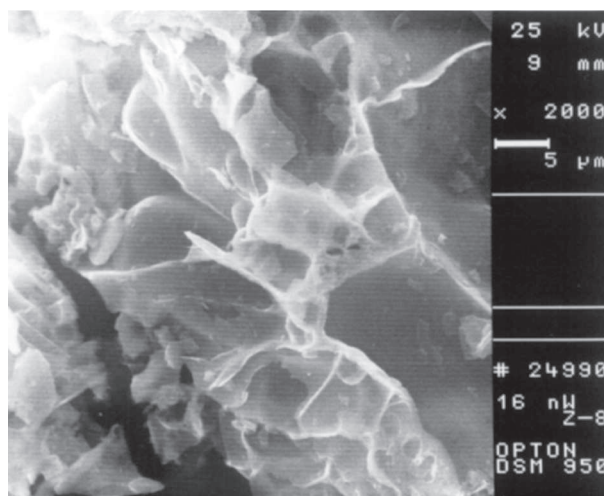


**Fig. 2.** XRD spectra of the YAG powders calcined in different temperatures: 1 – 120°C; 2– 800°C; 3 – 1000°C; 4 – 1000°C (4% mol  $\text{Nd}_2\text{O}_3$ ).

**Rys. 2.** Widma XRD proszków YAG kalcynowanych w różnych temperaturach: 1 – 120°C; 2 – 800°C; 3 – 1000°C; 4 – 1000°C (4% mol  $\text{Nd}_2\text{O}_3$ ).

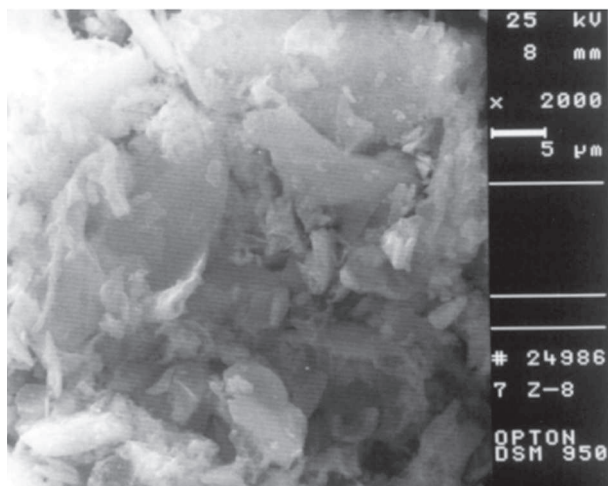
The parent xerogel diffractogram (spectrum 1, Fig. 2) has form of the line parallel to the abscissa. The diffractogram of the powder treated with 800°C (spectrum 2, Fig. 2) exhibits a sole small peak at  $2\theta$  equal to ca. 33.5°. Thermal treatment of the YAG xerogel and Nd-doped YAG at temperatures exceeding 1000°C results in generation of numerous peaks which do not change in presence of  $\text{Nd}_2\text{O}_3$  amounts above 4% (spectra 3 - 4, Fig. 2). Comparison of the diffractograms obtained with those originating from nanocrystalline YAG has proven that we deal with polycrystalline YAG powders with lattice constants range from 1.1979 nm to 1.2007 nm, and crystallite sizes from 107 nm to 310 nm.

The scanning microscope snaps of the YAG xerogels after temperature treatment at 800°C and 1200°C are presented in Figs. 3–5. The xerogel microstructure is formed from shapeless flakes with sharp edges of the size of  $5\ \mu\text{m} - 35\ \mu\text{m}$  (Fig. 3). The gradual heat of the sample to 800 °C and keeping it at this temperature for two hours (Fig. 4) yields change of the sample color from yellowish to dark brown, however, the color changes is not reflected in observable microstructure changes.



**Fig. 3.** Shape and surface morphology of the particles YAG xerogel after drying at 120°C during 6 hours.

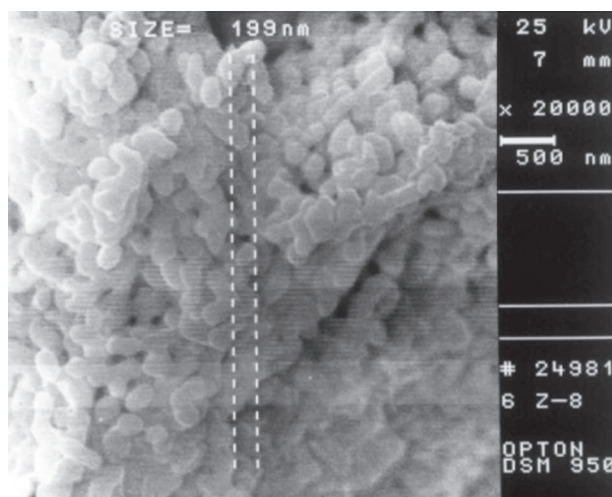
**Rys. 3.** Kształt i morfologia powierzchni cząsteczek kszerogelu YAG wysuszonego w ciągu 6 godzin w temperaturze 120°C.



**Fig. 4.** Surface morphology and size of the particles YAG powder calcined at 800°C during 2 hours.

**Rys. 4.** Kształt i morfologia powierzchni proszku YAG kalcynowanego w ciągu 2 godzin w temperaturze 800°C.

The further calcination of the powder at temperatures exceeding 1000°C for two to six hours leads to important changes of the powder microstructure (Fig. 5). The samples transform from amorphous to polycrystalline structure and small grains of spherical shape agglomerate. The approximate grain size is equal to 200 nm.

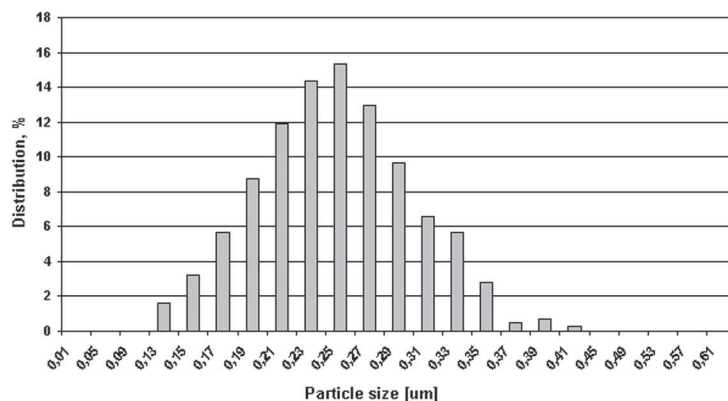


**Fig. 5.** Surface morphology, shape and size of the particles YAG powder after calcination at 1200°C during 2 hours.

**Rys. 5.** Morfologia powierzchni, kształt i rozmiary cząsteczek proszku YAG kalcynowanego w ciągu 2 godzin w temperaturze 1200°C.



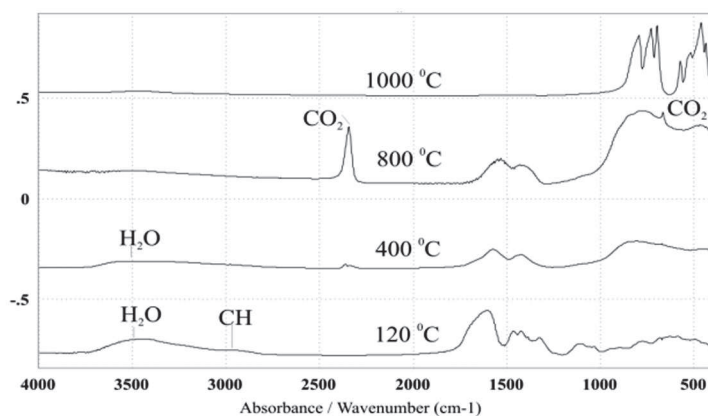
More detailed analysis of the particle size and the size distribution was obtained from Clemex TV image analyzer (Figs. 5 - 6). It appeared that more than half of the particles (54.6%) have size in the range of 200 nm – 300 nm, and the mean particle size is equal to 254 nm  $\pm$  47 nm.



**Fig. 6.** Particle size distribution of YAG powder after calcination at 1200°C during 2 hours.

**Rys. 6.** Rozkład rozmiarów cząsteczek proszku YAG kalcynowanego w ciągu 2 godzin w temperaturze 1200°C.

The IR spectra of the xerogels dried at 120°C and next thermally treated at 400°C, 800°C and 1000°C are presented in Fig. 7. Analysis of the IR spectra shows



**Fig. 7.** IR spectra of the xerogels dried at 120°C and next calcinated in different temperatures during 2 hours.

**Rys. 7.** Widmo IR kserożelu wysuszonego w 120°C, a następnie kalcynowanego w ciągu 2 godzin, w różnych temperaturach.

that parent xerogel absorb intensively at  $3444\text{ cm}^{-1}$ ,  $2954\text{ cm}^{-1}$ , and in the range of  $1400\text{ cm}^{-1}$ –  $1700\text{ cm}^{-1}$ . The sample annealing at  $400^\circ\text{C}$  for two hours leads to almost entire removal of the bands at  $3444\text{ cm}^{-1}$  and  $2954\text{ cm}^{-1}$ , and decrease of the absorptions at the range of  $1400\text{ cm}^{-1}$ –  $1700\text{ cm}^{-1}$ . The temperature treatment at  $800^\circ\text{C}$  for two hours leads to removal of the bands the range of  $4000\text{ cm}^{-1}$  –  $2500\text{ cm}^{-1}$ , and to further intensity decrease of the bands at  $1422\text{ cm}^{-1}$  and  $1532\text{ cm}^{-1}$  with simultaneous formation of a band at  $2342\text{ cm}^{-1}$ . Annealing at  $1000^\circ\text{C}$  result in removal of all bands but those below  $1000\text{ cm}^{-1}$ .

## 5. DISCUSSION

The formation of polycrystalline powder of yttrium aluminum garnet structure is complex and proceeds via several stages [1-10]. This is the case in this study, too. The YAG xerogel dried in  $120^\circ\text{C}$  contains metal ions, nitric acid and acetic acid counterions and ethylene glycol, the moieties, which are linked between each other through the chemical bonds. The IR absorption bands at  $3444\text{ cm}^{-1}$  and  $2954\text{ cm}^{-1}$  (Fig. 7) indicate presence of water and CH moieties. Inspection into IR spectra of yttrium acetate and aluminium nitrate shows that the bands in the  $1400\text{ cm}^{-1}$ –  $1700\text{ cm}^{-1}$  region can be assigned univocally to acetates.

Based on absence of any bands at the diffractogram 1 (Fig. 2) one can state that the parent YAG xerogel is amorphous. Also, this is in line with photographs taken by using electron microscopy technique (Fig. 3). Thermal analysis (Fig. 1) indicates, that the 4.4% mass lost during the low-temperature (below  $400^\circ\text{C}$ ) stage of the xerogel pyrolysis is connected with the endothermic lost of water molecules. The mass lost in the temperature range  $200^\circ\text{C}$  –  $400^\circ\text{C}$  and the exothermic effect connected with it with maximum at  $380^\circ\text{C}$  are likely to be associated with partial burning of organic xerogel components. Indeed, the IR spectrum of the sample calcinated at  $400^\circ\text{C}$ , in which bands in the  $4000\text{ cm}^{-1}$ –  $2500\text{ cm}^{-1}$  region are much less intense than these registered for lower temperatures, confirms the above supposition. The slight mass increase and exothermic effect accompanying to it in the temperature range of  $600^\circ\text{C}$  –  $840^\circ\text{C}$ , is probably due to two processes: further thermal destruction and simultaneous  $\text{CO}_2$  adsorption. This is confirmed by detection of the  $2342\text{ cm}^{-1}$  band assigned to the antisymmetric stretching vibrations of carbon dioxide. However, as indicated at the diffractogram of the sample burned at  $800^\circ\text{C}$  (Fig. 2, spectrum 2), this very temperature is insufficient to form a YAG crystalline precursor: the diffractogram of the powder indicates that amorphous xerogel structure did not undergo changes. The same conclusion can be drawn based on the appropriate electron microscope image (Fig. 4).

The second high heat effect, seen as a maximum in the DTA curve at 858°C, and the 6.6% mass lost smaller than that for the reaction at 380°C is connected with process of the organic remaining burning, desorption of CO<sub>2</sub>, and phase change during which a polycrystalline powder of yttrium aluminum garnet is formed. As a result of the phase change, in the diffractograms (spectra 3 – 4, Fig. 2) peaks characteristic for the YAG monocrystals appear. The electron microscope photograph (Fig. 5) confirms that rising of temperature produces the amorphous xerogel transformation into small, well shaped particles, with narrow size distribution. The FTIR spectrum of the powder calcinated at 1000°C (Fig. 7) exhibits absorption bands in the range below 1000 cm<sup>-1</sup>, only. These bands are characteristic for the Me – O stretching and bending vibrations.

The physico-chemical methods applied for investigation of polycrystalline yttrium aluminum garnet precursor formation enable us to propose the following mechanism of the process.

The process starts with dissolution of yttrium and neodymium oxides in acetic acid:



The yttrium and neodymium acetates formed as well as aluminum nitrate undergo dissociation into ions:

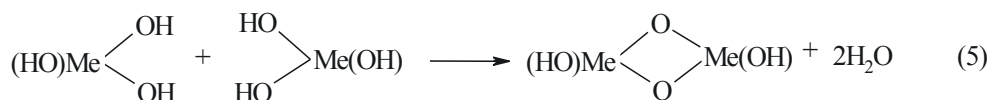


The elevated temperature and weak acidic environment cause hydrolysis and yttrium, neodymium and aluminum hydroxides are produced:



where Me stands for Y, Nd or Al.

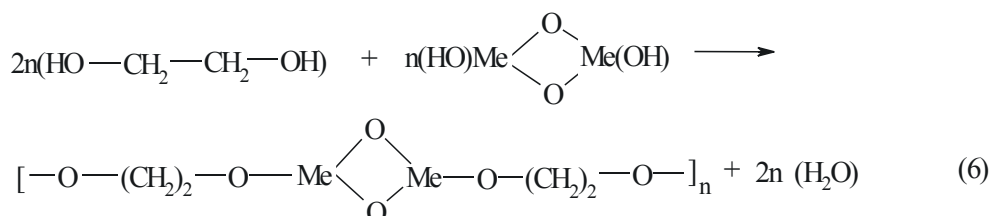
The hydroxides undergo olation and the metal atoms become to be bound by the oxygen bridges:



The ethylene glycol added plays an important role: each ethylene glycol molecule can bind the oxygen bridged metal compounds through the two hydroxide groups

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into polymers with relatively small mer-repetition number  $n$ . As a result, a matrix influencing precursor molecule size appears:



During a cautious calcination (temperature increase slower than 2°C/min) this very matrix protects system from too early interaction between oxygen and metal atoms, which would lead to formation of separate yttrium, neodymium and aluminum oxides compounds which could unable to reach the aim - production of the powder with the YAG structure being the solid solution of the  $\text{Y}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  oxides.

## 6. CONCLUSIONS

As a result of this study aiming production of the laser YAG:Nd ceramics by using the sol-gel method the following was performed:

The base for technology of the laser yttrium aluminum garnet ceramics in form of the  $[\text{Y}_3\text{Al}_2(\text{AlO}_4)_3]$  compound doped with the Nd atoms by using the sol-gel method was described. The glycolate method known from the literature [24] was developed for obtaining powders of YAG highly doped by neodymium (up 28% AT.).

It was established that the xerogel particles calcinated at temperatures above 800°C show the desired YAG structure.

The desired monocrystalline garnet structure of the obtained product was confirmed by using the X-ray diffraction method and scanning electron microscopy.

Based on the thermal analysis and IR spectroscopy methods the low-temperature stages of the thermo-destruction of the xerogel dried at 120°C were examined.

Finally, the mechanism of the yttrium aluminum garnet powder formation by the sol-gel method was proposed.

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## SUMMARY

### **BADANIE PROCESÓW ZOL-ŻEL ZACHODZĄCYCH PRZY WYTWARZANIU NANOKRYSTALICZNYCH PROSZKÓW GRANATU ITROWO ALUMINIOWEGO**

Metodę zol-żel wykorzystano do otrzymywania nanokrystalicznych granatów YAG i YAG:Nd. Przedstawiono mechanizm powstawania proszków o krystalicznej strukturze granatu. Odpowiednie żele otrzymywano w reakcji nieorganicznych soli lub tlenków pierwiastków Y, Al, Nd z kwasem octowym i glikolem etylenowym. Poszczególne etapy procesu zol-żel oraz reakcje zachodzące podczas obróbki termicznej kserożeli w zakresie od 100°C do 1000°C badano metodami: analizy termicznej DTA, dyfrakcji rentgenowskiej XRD, oraz spektroskopii w podczerwieni IR. Rozmiar, kształt oraz morfologię powierzchni proszków charakteryzowano za pomocą skaningowej mikroskopii elektronowej SEM. Otrzymano jednofazowe proszki czystego granatu YAG i domieszkowanego neodymem w ilościach aż do 28%. Dla wyższych zawartości neodymu (do 100%) obserwowano występowanie dwóch faz - granatu i perowskitu.