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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 100^0C to 1000^0C 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, homogenicity 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 homogenicity 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 enterapped 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 monocrystallic 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^{o}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^{o}C -1200^{o}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^{o}C, into solid xerogels. The polycrystalline YAG precursor powders are formed as a result of thermal treatment - calcination at 1000^{o}C [20-22].

Precursors of YAG nanocrystals can be obtained by two routs 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^{o}C – 60^{o}C. During the curse 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 $Al(NO)_3 \cdot 9\ H_2O$ 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^{o}C – 70^{o}C, the agitated solution containing Y, Al, acetate, nitrate, and glycol, transformed into a white-transparent gel, which after drying at 100^{o}C – 120^{o}C changed its color into brownish. The dried xerogel powder was size-reduced within two hours at 800^{o}C in the air atmosphere. Because, organic compounds containing gels are flammable, the slow temperature increase (ca. 2^o/min) was applied, especially in the temperature range of 150^{o}C – 400^{o}C. After, the additional size-reduction, the powders were six hours calcinated at 800^{o}C – 1600^{o}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_2O_3 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_2O_3 mass (g)	Y_2O_3 mass (g)	$Al.(NO_3)_3 \cdot 9\ H_2O$ 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 diffractometr 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°C – 65°C, acquisition time of 4 s, and Cu K_α 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^{-1}– 400 cm^{-1}) were recorded by using the Perkin-Elmer System 2000 FTIR spectrometer with 4 cm^{-1} 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^{o}C-1000^{o}C is presented in Fig. 1. The upper curve (TGA) reflects

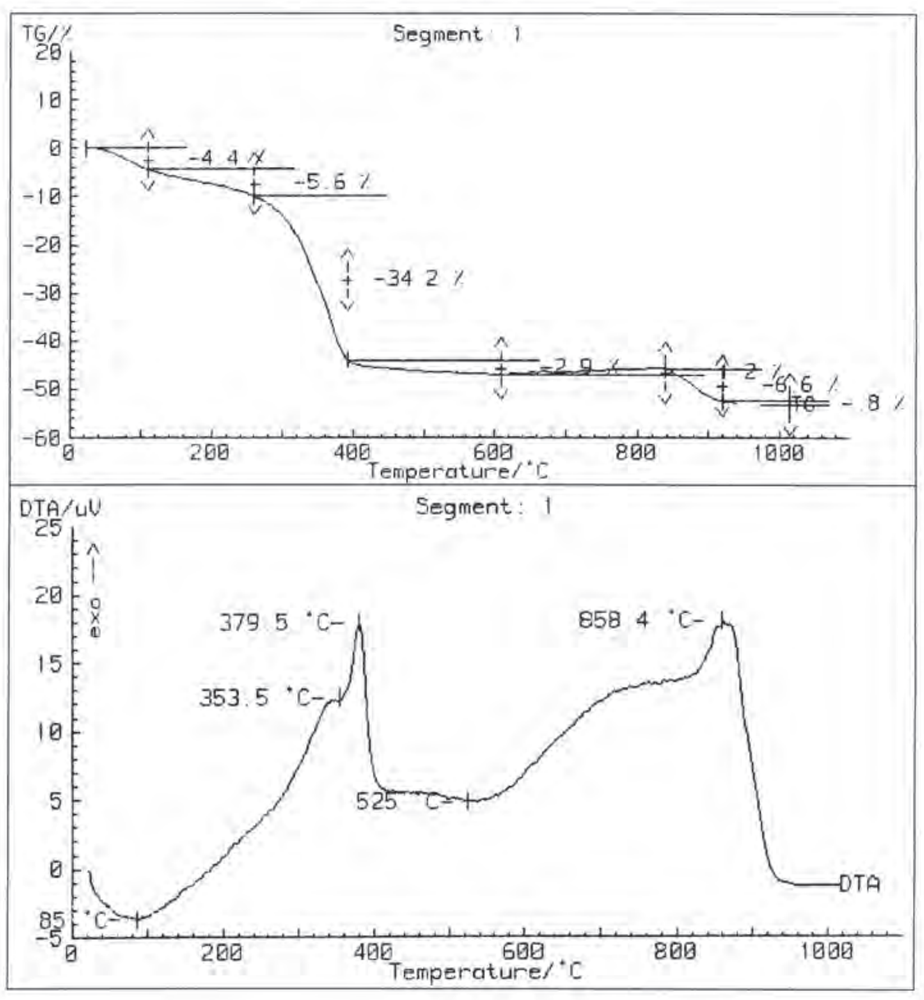


Fig. 1. TGA and DTA curves of YAG xerogels, temperature increase of 2^{o}C/min.
Rys.1. Krzywe TGA i DTA wykonane dla kserożelu YAG, wzrost temperatury 2^{o}C/min.

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 egzothermic processes. The largest heat effect at temperature equal to 379^{o}C comes with the largest mass attenuation of 34.2%. In the temperature range 600^{o}C – 840^{o}C one can observe a slight mass increase, a matter of 1.2%, and a slightly egzothermic reaction. The second high heat effect reaches its maximum at 858^{o}C, however, the accompanying mass decrease is lower than that at 379^{o}C and is equal to 6.6%.

The dependence of the X-ray lines of the YAG powders on the 2θ 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 Nd_2O_3 thermal treated in different temperatures.

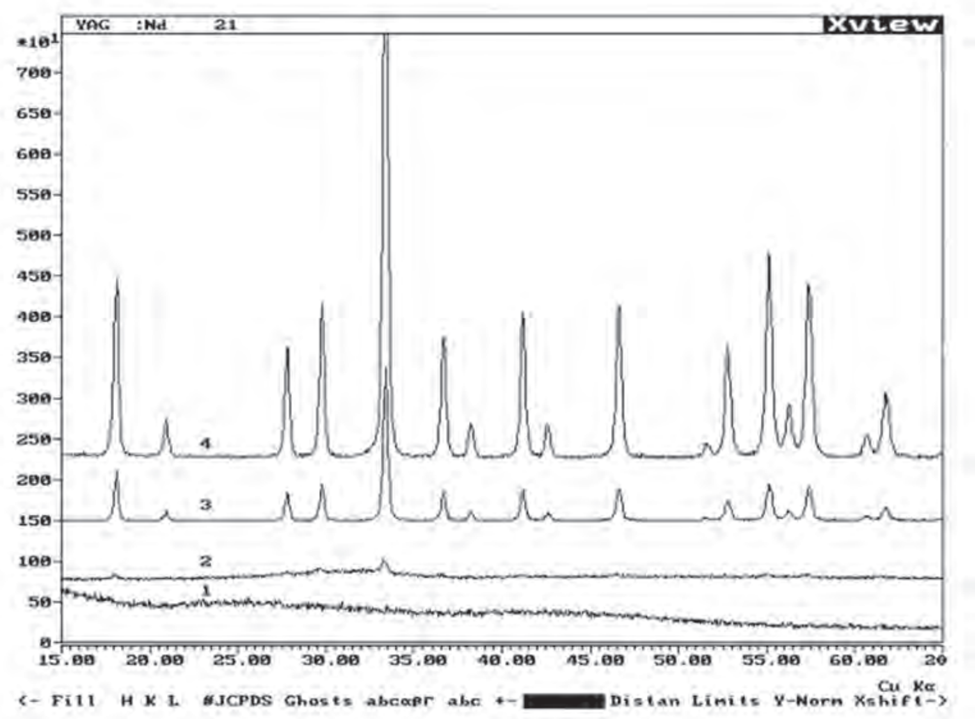


Fig. 2. XRD spectra of the YAG powders calcined in different temperatures: 1 – 120^{o}C; 2– 800^{o}C; 3 – 1000^{o}C; 4 – 1000^{o}C (4% mol Nd_2O_3).
Rys. 2. Widma XRD proszków YAG kalcynowanych w różnych temperaturach: 1 – 120^{o}C; 2 – 800^{o}C; 3 – 1000^{o}C; 4 – 1000^{o}C (4% mol Nd_2O_3).

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 2θ equal to ca. 33.5°. Thermal treatment of the YAG xerogel and Nd-doped YAG at temperatures exceeding 1000⁰C results in generation of numerous peaks which do not change in presence of Nd_2O_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 μ – 35 μ (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.

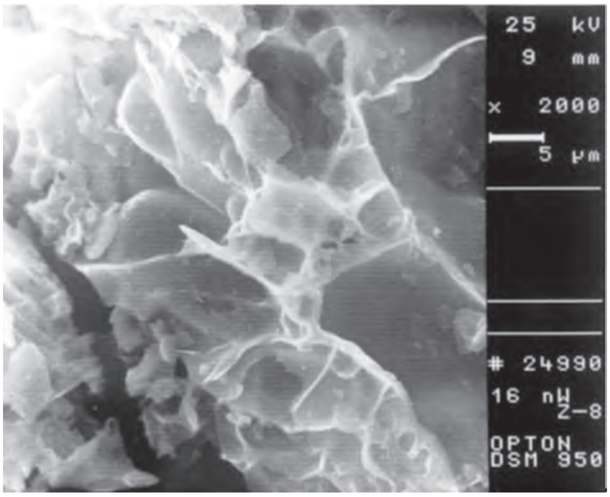


Fig. 3. Shape and surface morphology of the particles YAG xerogel after drying at 120°C during 6 hours.
Rys. 3. Kształt i morfologia powierzchni cząsteczek kserożelu YAG wysuszonego w ciągu 6 godzin w temperaturze 120°C.

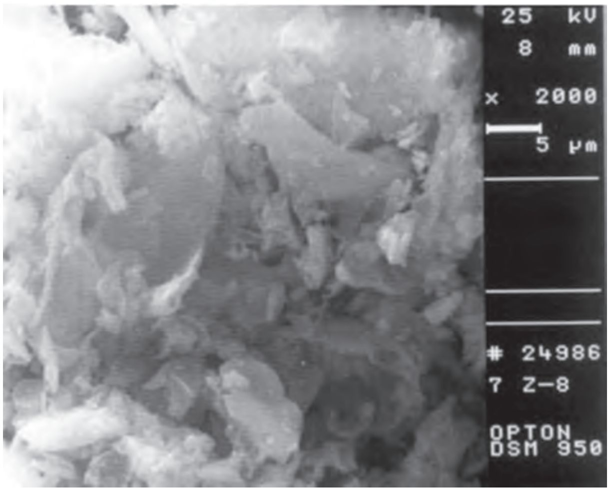


Fig. 4. Surface morphology and size of the particles YAG powder calcined at 800^{o}C during 2 hours.

Rys. 4. Kształt i morfologia powierzchni proszku YAG kalcynowanego w ciągu 2 godzin w temperaturze 800^{0}C.

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

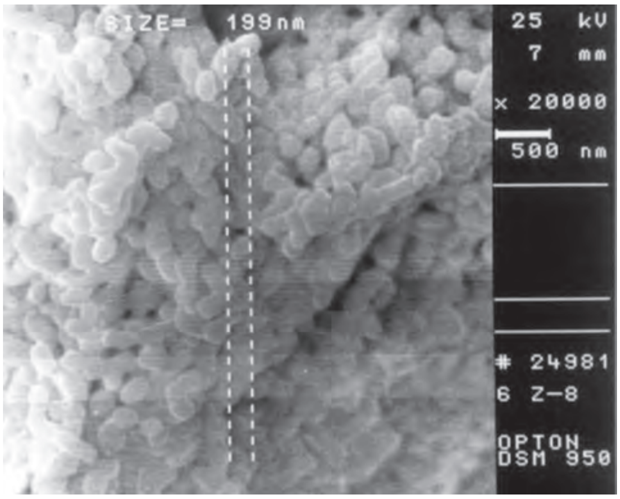


Fig. 5. Surface morphology, shape and size of the particles YAG powder after calcination at 1200^{o}C during 2 hours.

Rys. 5. Morfologia powierzchni, kształt i rozmiary cząsteczek proszku YAG kalcynowanego w ciągu 2 godzin w temperaturze 1200^{o}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 then 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 ± 47 nm.

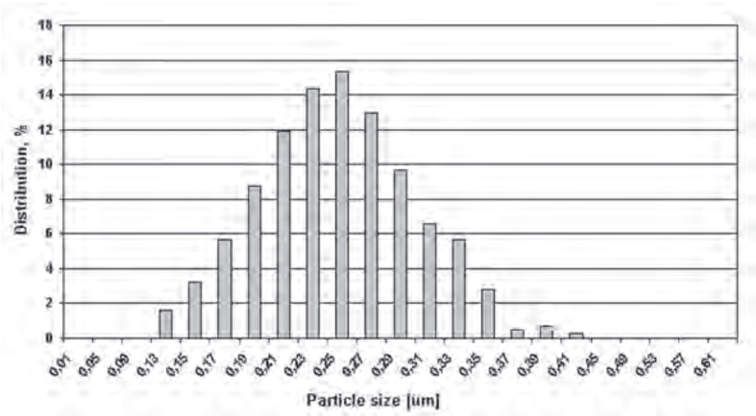


Fig. 6. Particle size distribution of YAG powder after calcination at 1200°C during 2 hours.
Rys. 6. Rozkład rozmiarów cząsteczek proszku YAG kalcynowanego w ciągu 2 godzin w temperaturze 1200°C.

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

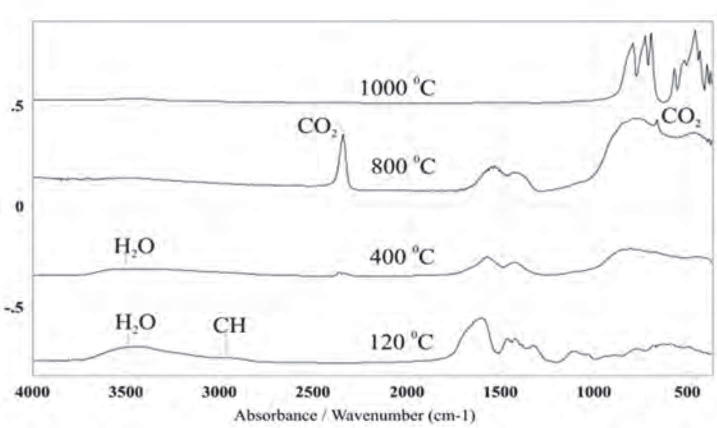


Fig. 7. IR spectra of the xerogels dried at 120°C and next calcinated in different temperatures during 2 hours.
Rys. 7. Widmo IR kserożelu wysuszonego w 120°C, a następnie kalcynowanego w ciągu 2 godzin, w różnych temperaturach.

that parent xerogel absorb intensively at 3444 cm^{-1}, 2954 cm^{-1}, and in the range of 1400 cm^{-1}– 1700 cm^{-1}. The sample annealing at 400°C for two hours leads to almost entire removal of the bands at 3444 cm^{-1} and 2954 cm^{-1}, and decrease of the absorptions at the range of 1400 cm^{-1}– 1700 cm^{-1}. The temperature treatment at 800°C for two hours leads to removal of the bands the range of 4000 cm^{-1} – 2500 cm^{-1}, and to further intensity decrease of the bands at 1422 cm^{-1} and 1532 cm^{-1} with simultaneous formation of a band at 2342 cm^{-1}. Annealing at 1000°C result in removal of all bands but those below 1000 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°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 cm^{-1} and 2954 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 cm^{-1}– 1700 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°C) stage of the xerogel pyrolysis is connected with the endothermic lost of water molecules. The mass lost in the temperature range 200°C – 400°C and the exothermic effect connected with it with maximum at 380°C are likely to be associated with partial burning of organic xerogel components. Indeed, the IR spectrum of the sample calcinated at 400°C, in which bands in the 4000 cm^{-1}– 2500 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°C – 840°C, is probably due to two processes: further thermal destruction and simultaneous CO_2 adsorption. This is confirmed by detection of the 2342 cm^{-1} band assigned to the antisymmetric stretching vibrations of carbon dioxide. However, as indicated at the diffractogram of the sample burned at 800°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_2, 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^{-1}, 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:

$$Y_2O_3 + 6\ CH_3COOH = 2\ Y(CH_3COO)_3 + 3\ H_2O \qquad (1a)$$
$$Nd_2O_3 + 6\ CH_3COOH = 2\ Nd(CH_3COO)_3 + 3\ H_2O \qquad (1b)$$

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

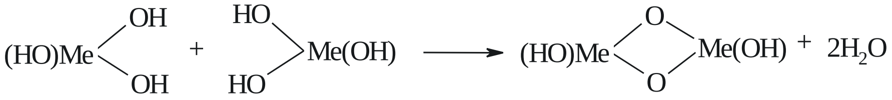
$$Y(CH_3COO)_3 = Y^{3+} + 3\ CH_3COO^- \qquad (2a)$$
$$Nd(CH_3COO)_3 = Nd^{3+} + 3\ CH_3COO^- \qquad (2b)$$
$$Al(NO_3)_3 = Al^{3+} + 3\ NO_3^- \qquad (3)$$

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

$$Me^{3+} + 3\ HOH = Me(OH)_3 \qquad (4),$$

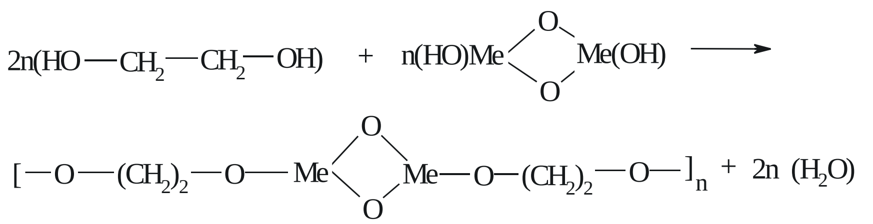
where Me stands for Y, Nd or Al.

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



(5)

The ethylene glycol added plays an important role: each ethylene glycol molecule can bind the oxygen bridged metal compounds through the two hydroxide groups into polymers with relatively small mer-repetition number *n*. As a result, a matrix influencing precursor molecule size appears:



(6)

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 Y_2O_3, Nd_2O_3 and Al_2O_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 $[Y_3Al_2(AlO_4)_3]$ 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 800^0C 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 120^0C were examined.

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

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REFERENCES

[1] Uhlmann D.R., Boulton J.M., Teowee G.: New optical materials by wet chemical processing, *J. Non-Cryts. Solids*, 196, 1996 26-36

[2] Brinker C.J., Scherer G.W.: Sol-gel science: The physics and chemistry of sol-gel processing. Academic Press, New York, 1990

[3] Wright J.D., Sommerdijk A.J.M.: Sol-gel materials: chemistry and applications, Gordon and Breach Science Publishers, The Netherlands, 2001

[4] Reifeld R.: Prospects of sol-gel technology towards luminescent materials. *Opt. Mater.* 16, 2001, 1-7

[5] Livage J.: Sol-gel processes, Current Opinion in *Solid State and Materials Science,* 2, 1997, 132-138

[6] Bhandarkar S.: Sol-gel processing for optical communication technology, *J. Am. Ceram. Soc.*, 87 ,7, 2004, 1180-1199

[7] Cheng S.D. et al.: Fluorescence properties of Er^{3+}: $LiNbO_3$ sol-gel powder. *Materials Letters*, 45, 2000, 19-22

[8] Cheng S.D. et al.: Fluorescence properties of Nd^{3+}: $LiNbO_3$ sol-gel derived powders. *Materials Letters*, 48, 2001, 369-373

[9] Legendziewicz J., Stręk W., Sokolnicki J., Hreniak D., Zolin V.: Optical properties of Nd^{3+} in silica ceramics obtained by the sol-gel method. *Opt. Mater.*, 19, 2002, 175-181

[10] Hreniak D., Stręk W., Mazur P., Pazik R., Ząbkowska-Wacławek M.: Luminescence properties of Tb^{3+}:$Y_3Al_5O_{12}$ nanocrystallites prepared by the sol-gel method, *Opt. Mater.* 26, 2004, 117-121

[11] Muliuoliene I. et al.: Evidence of the formation of mixed-metal garnets via sol-gel synthesis. *Opt. Mater.* 22, 2003, 241-250

[12] Pullar R.C., Taylor M.D., Bhattacharya A.K.: The zintering behaviour, mechanical properties and creep resistance of aligned polycrystalline ytrium aluminium garnet (YAG) fibres, Produced from an Aqueous Sol-Gel Precursor. *J. Europ. Ceram. Soc.*,. 19, 1999, 1747-1758

[13] Pullar R.C., Bhattacharya A.K.: Polycrystalline yttrium aluminium Garnet (YAG) fibres produced from the steaming of an aqueous sol-gel precursor. *Materials Letters* 39, 1999, 173-178

[14] Ikesue A.: Polycrystalline Nd:YAG ceramics lasers. *Optical Materials*,19, 2002, 183-187

[15] Ikesue A., K. Kamata, K. Yoshida, Effects of neodymium concentration on optical characteristics of polycrystalline Nd:YAG laser materials. *J. Am. Ceram. Soc.*, 79,7, 1996, 1921-26

[16] Rabinovitch Y.,Tetard D., Faucher M.D.: Pham-Thi M.: Transparent polycrystalline neodymium doped YAG: synthesis parameters, laser efficiency, 24, 2003, 345-351

[17] Lu J., Ueda K., Yagi H., Yanagitani T., Akiyama Y., Kaminskii A.A.: Neodymium doped yttrium aluminium Garnet ($Y_3Al_5O_{12}$) nanocrystalline ceramics-a new generation. *Solid State Laser and Optical Materials,* 341, 2002, 220-225

[18] Wen L., Sun X., Xiu Z., Chen S., Tsai C.: Synthesis of nanocrystalline yttria powder and fabrication of transparent YAG ceramics. *Journal of the European Ceramic Society*, 24, 2004, 2681-2688

[19] Matsushita N., Tsuchiya N., Nakatsuka K., Yanagitani T.: Precipitation and calcination processes for yttrium aluminum garnet precursors synthesized by the urea method. *J. Am. Ceram. Soc*., 82, 8, 1999, 1977-84

[20] Liu Y., Zhang Z.F., King B., Holloran J., Laine R.M.: Synthesis of yttrium aluminum garnet from yttrium and aluminum isobutyrate precursors. *J. Am. Ceram. Soc.*, 79, 2, 1996, 385-94

[21] Vagueiro P., López-Quintela A.M.: Synthesis of yttrium aluminium garnet by the citrate gel process. *J. Mater. Chem*., 8, 1, 1998, 161 – 163

[22] Chung B.J., Park J.Y., Sim S.M.: Synthesis of yttrium aluminum garnet powder by a citrate gel method. *J. Cer. Process. Res*., 4, 3, 2003, 145-150

[23] Chinie A.M., Stefan A., Georgescu S.: Synthesis by a citrate sol-gel method and characterization of Eu^{3+}-doped yttrium aluminum garnet nanocrystals. *Romanian Reports in Physics*, 57, 3, 2005, 412-417

[24] Veith M., Mathur S.., Kareiva A., Julavi M., Zimmer M., Huch V.: Low temperature synthesis of nanocrystalline $Y_3A_5O_{12}$ (YAG) and Ce-Doped $Y_3A_5O_{12}$ via different sol--gel methods. *J. Mater. Chem.,* 9, 1999, 3069 – 3079

[25] De la Rosa E., et al: Low temperature synthesis and structural characterization of nanocrystalline YAG prepared by a modified sol-gel method. *Opt. Mater.,* 27, 2005, 1793-1799

[26] Wang S., Xu Y., Lu P., Xu C., Cao W.: Synthesis of yttrium aluminum garnet YAG from ethylenediaminetetraacetic acid precursor. *Mater .Sci. Eng. B*, 127, 2006, 203-206

[27] Harada M., Goto M.: Synthesis of Y-Al-O compounds by a polymer complex method. *J. Alloys Compounds*, 408-412, 2006, 1193-1195

[28] Lipinska L., Lojko L., Kłos A., Ganschow S., Diduszko R.,Ryba-Romanowski W., Pajączkowska A.: Solubility and physicochemical properties of nanopowders and crystalline solids in the $(Y_{1-}xNd_x)_3Al_5O_{12}$ system. *J. Alloys Comp*., 2006 in press.

SUMMARY

BADANIE PROCESÓW ZOL-ŻEL ZACHODZĄCYCH PRZY WYTWARZANIU NANOKRYSZTALICZNYCH 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 100^0C do 1000^0C 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.