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Crystal structure and luminescent properties of nanocrystalline YAG and YAG:Nd synthesized by sol–gel method

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ABSTRACT

The work describes results of synthesis of undoped and Nd-doped YAG nanopowders by sol–gel method using different complexing agents (ethylene glycol and citric acid) and characterization of the material by X-ray powder diffraction, scanning electron microscopy, photoluminescence and thermoluminescence techniques. Utilization of citrate sol–gel procedure using yttrium and aluminum nitrate nonahydrates as starting substances allowed to obtain highly stoichiometric and non-defected YAG and YAG:Nd nanocrystalline samples with good luminescence performance and low radiation storage efficiency.

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1. Introduction

Yttrium aluminum garnet (YAG) optically transparent ceramics activated with rare-earth or transition metal ions is one of the most perspective nowadays materials for light emitting devices [1]. The most optimal technology for production of nanocrystalline powder for such ceramics is a sol–gel method excluding complicated and power-consuming manufacturing operations [2,3].

Besides, it has been recently shown that undoped and rare-earth doped nanocrystalline YAG have good radiation storage properties that make them applicable for ionizing radiation dosimetry using thermally- or optically stimulated luminescence technique [4,5]. The thermally stimulated luminescence is also an efficient experimental tool to study intrinsic and extrinsic point defects of the lattice by observation of trapping and recombination processes, in which these defects participate.

Therefore the purpose of the present work was a sol–gel synthesis of undoped and Nd-doped YAG nanopowders and their characterization by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), photoluminescence (PL) and thermoluminescence (TL) techniques.

2. Experimental procedures

The studied YAG and Nd-doped YAG nanopowders have been synthesized by two well-known modifications of sol–gel method – glycol and citrate ones. In the glycol sol–gel method following substances were used: aluminum nitrate nonahydrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, yttrium oxide Y_2O_3 and neodymium oxide Nd_2O_3 , nitric acid HNO_3 65%, acetic acid CH_3COOH , ethylene glycol $\text{C}_2\text{H}_6\text{O}_2$ and distilled water H_2O . In the citrate sol–gel method following substances were used: yttrium nitrate nonahydrate $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and aluminum nitrate nonahydrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, neodymium oxide Nd_2O_3 , nitric acid HNO_3 65%, citric acid $\text{C}_6\text{H}_8\text{O}_7$ and distilled water H_2O . Amounts of reagents used in both synthesis procedures are listed in Table 1.

In glycol sol–gel procedure, Y_2O_3 was dissolved in 200 ml of HNO_3 in magnetic stirrer during 2 h at temperature between 50 and 60 °C, after that 7.5 ml of acetic acid was added. As-obtained solution was opaque and white in color. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 85 ml of H_2O and kept at room temperature during 30 min. This solution was added to the previous one and the mixture was aged at 60 °C for obtaining a fully transparent solution. At the end, 8.8 ml of ethylene glycol was added. During aging at 70 °C, sol containing yttrium and aluminum nitrates and acetates was transformed into a transparent gel, which after drying at 120 °C during 4–5 h have been changed in color into light-brownish and increased in volume in 4–5 times.

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Table 1
Amounts of Y, Nd, and Al compounds used for obtaining 10 g Nd-doped YAG nanopowders.

| Nd concentration (mol.%) | Nd ₂ O ₃ (g) | Y ₂ O ₃ (g) | Y(NO ₃) ₃ ·6H ₂ O (g) | Al(NO ₃) ₃ ·9H ₂ O (g) |
|--------------------------|------------------------------------|-----------------------------------|---|--|
| 1 | 0.0850 | 5.6498 | 19.16582 | 31.597 |
| 2 | 0.17 | 5.591 | 18.96635 | 31.597 |
| 3 | 0.2551 | 5.5351 | 18.77672 | 31.597 |
| 4 | 0.3363 | 5.4171 | 18.37643 | 31.247 |

Table 2
List of the YAG samples studied in the work.

| Sample (notation) | Synthesis modification | Calcination temperature (°C) | Phase composition | Average size of crystallites (<i>D</i>) and microstrain (ϵ) | | | Parameter of YAG unit cell (Å) |
|-------------------------|------------------------|------------------------------|-----------------------|--|---|---|--------------------------------|
| | | | | <i>D</i> _{Sh} ^a (nm) | <i>D</i> _{W-H} ^b (nm) | $\langle\epsilon\rangle = \langle\Delta d\rangle/d$ (%) | |
| YAG (Ct001) | Egl | 1000 | YAG (67%) + YAM (33%) | 80–117 | 144 | 0.07 | 12.025(2) |
| YAG:Nd 1 mol.% (Ct002) | Egl | 1000 | YAG (68%) + YAM (32%) | | | | 12.025(3) |
| YAG:Nd 2 mol.% (Ct003) | Egl | 1000 | YAG (65%) + YAM (35%) | | | | 12.028(2) |
| YAG:Nd 3 mol.% (Ct004) | Egl | 1000 | YAG (51%) + YAM (49%) | | | | 12.028(2) |
| YAG:Nd 4 mol.% (Ct005) | Egl | 1000 | YAG (70%) + YAM (30%) | 63 | 109 | 0.13 | 12.036(2) |
| YAG (Ibg01) | CAC | 900 | YAG | 36 | 50 | 0.15 | 12.017(7) |
| YAG:Nd 1 mol.% (Ct010) | CAC | 1000 | YAG | 80–110 | 253 | 0.11 | 12.037(1) |
| YAG (Ct022) | CAC | 1000 | YAG | 39 | 59 | 0.14 | 12.015(2) |
| YAG (Ct022a) | CAC | 1200 | YAG | 230 | 450 | 0.059 | 12.0041(6) |
| YAG:Nd 1 mol.% (Ct023) | CAC | 1000 | YAG | 48 | 118 | 0.21 | 12.022(1) |
| YAG:Nd 1 mol.% (Ct023a) | CAC | 1200 | YAG | 120–130 | 171 | 0.033 | 12.0053(6) |

^a Average size of crystallites determined using the Scherrer's equation for first 3 reflections (122), (220) and (123) at 25.3°.

^b Average size of crystallites determined from the Williamson-Hall plot for 9(10) reflections in the 18–46° angle range.

In citrate sol–gel procedure, Y(NO₃)₃·6H₂O was dissolved in 50 ml of H₂O in magnetic stirrer during 1 h at room temperature. Al(NO₃)₃·9H₂O was dissolved in 50 ml of H₂O and kept at room temperature during 1 h. Both solutions were mixed together, kept at room temperature for 2 h, after that the citric acid was added. The ratio of nitrates to citric acid was 1:1. Obtained sol was aged at 5 °C during 24 h. Slow evaporation of sol containing mixture of Y and Al nitrates and citrates at 100–110 °C led to transformation into a transparent gel, which after drying at 200 °C during 1 h changed in color to light-brownish and increased in volume in 4–5 times.

To obtain the Nd-doped YAG, required amount of Nd₂O₃ was dissolved in 30 ml of HNO₃ and mixed with yttrium and aluminum containing solutions.

The dried xerogel powders obtained both by glycol and citrate sol–gel methods were size-reduced at 800 °C for 2 h, after that calcined at 900–1200 °C for 4 h in air. After finishing synthesis process, white YAG-based nanopowders were obtained.

Phase composition, crystal structure and microstructural characteristics of the samples were studied by means of X-ray powder diffraction (XRD) techniques. The measurements were performed using a PC interfaced DRON-3 M diffractometer with filtered Cu- or Co K α radiation in the 2 θ range of 10–90° (step-scan mode, $\Delta 2\theta = 0.02^\circ$). A qualitative phase analysis was performed by comparison of the experimental patterns with standard ones from the Powder Diffraction File PDF-2 of the International Centre for Diffraction Data (ICDD). Refinement of crystal structure parameters as well as quantitative phase analysis has been performed by full profile Rietveld method by using WinCSD program package [6].

The average size of crystallites was estimated from the line broadening by using of well-known Scherrer's equation, as well as by Williamson-Hall analysis [7], which allows to separate the effect of size and strain broadening due to their different dependence on the scattering angle. In both cases a LaB₆ external standard was used for determination of instrumental broadening of diffraction maxima.

A Hitachi SU-70 scanning electron microscope was used for SEM studies.

For luminescent studies, the pure YAG and YAG:Nd (from 1 to 4 mol.% Nd) samples were prepared as tablets of diameter 6 mm and thickness of 0.5 mm by pressing of the powders in a hydraulic press. Luminescent studies including measuring of photoluminescence (PL) spectra and decay kinetics were performed at room temperature using a nanosecond luminescence spectrometer NT342/3/C/UVF with a NT342/UV YAG:Nd laser system and Ge detector.

The thermoluminescent (TL) measurements of the samples were performed using a setup equipped with a compact furnace with programmable heating and a Triax 320 (Jobin Yvon-Spex) monochromator with a CCD camera. Application of the monochromator with CCD camera allowed to separate TL emission in a desired spectral region as well as to obtain spectra of TL emission during the TL experiments. For the thermoluminescent studies, the samples normally were stored and irradiated in darkness (wrapped in aluminum foil). Before each irradiation procedure the samples were annealed at 700 K during 15 min to erase any possible TL signal due to previous irradiation. Irradiation of the samples with γ -rays was performed at room temperature using a ⁶⁰Co sources with the dose rate ~ 0.8 kGy/h.

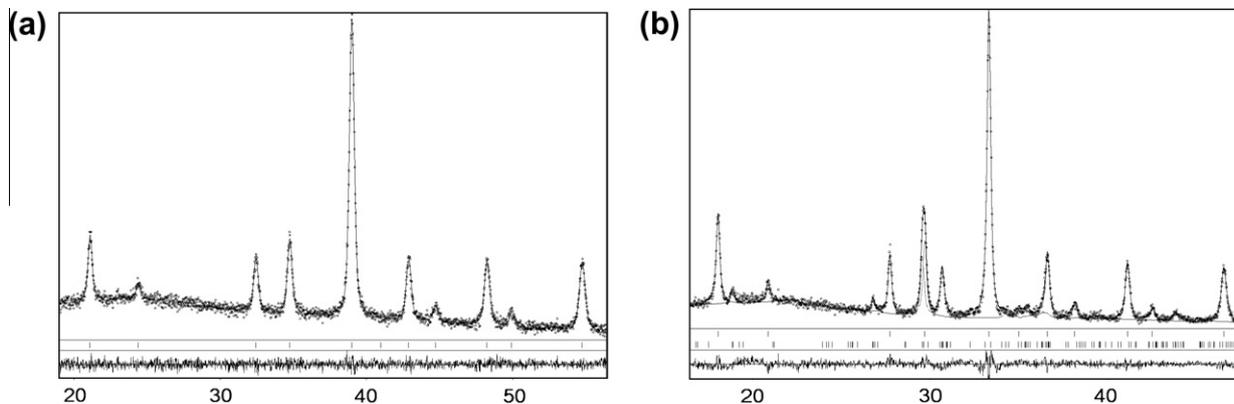


Fig. 1. Graphical results of Rietveld refinement of single-phase Ct022 (a) and two-phase Ct005 (b) specimens (Cu and Co $K\alpha$ -radiation, respectively). Experimental (points), calculated (continuous lines) and difference curves between experimental and calculated profiles are shown. Vertical bars indicate: in (a) – positions of diffraction maxima of YAG structure; in (b) – positions of maxima in YAG and YAM structures (upper and lower rows, respectively).

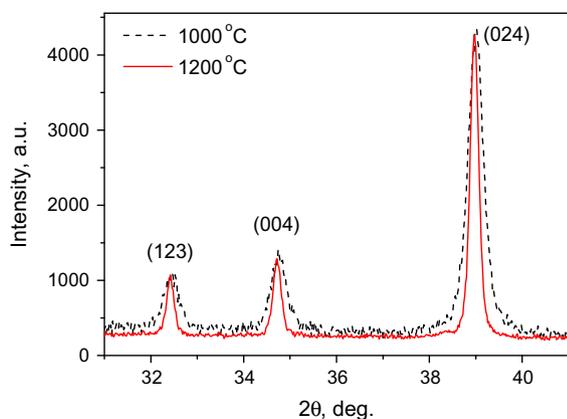


Fig. 2. Fragments of diffraction patterns of Ct022 YAG sample annealed at 1000 and 1200 °C showing narrowing of (123), (004) and (024) Bragg diffraction maxima.

3. Experimental results and discussion

3.1. Phase composition, crystal structure refinement and microstructure

X-ray diffraction examination revealed that the samples prepared using citric acid have pure garnet structure, whereas in the YAG and YAG:Nd samples prepared using ethylene glycol contain significant amount of $Y_4Al_2O_9$ (YAM) phase (Table 2). As example,

Fig. 1 shows the graphical results of the Rietveld refinement, proving single YAG phase and two-phase compositions of Ct022 and Ct005 samples, respectively.

Comparison of the refined values of the lattice parameters for pure and Nd-doped YAG samples, presented in Table 2 with the literature data for $Y_3Al_5O_{12}$ ($a = 12.009$ Å) show increase of the lattice parameters for Nd-containing specimens, which prove the partial substitution of larger neodymium atoms for yttrium sites in the garnet lattice.

We suppose that such drastic difference in the phase composition of samples obtained by different modifications of sol-gel procedures is caused not by the different complexing agents used, but possibly by the different starting substances. Namely, yttrium oxide was used in the glycol sol-gel procedure, while yttrium nitrate nonahydrate was used in the citrate procedure.

The average size of crystallites calculated using the Scherrer's equation was estimated to be from 36 to 110 nm for the samples calcined at 1000 °C (see Table 2). However, these values are somewhat underestimated due to additional broadening of diffraction peaks caused by microstrains (vacancies, site-disorder, etc.). To separate these two effects, angular dependency of integral breadth of diffraction maxima has been analyzed according to Williamson-Hall approach. According to this data, the average size of crystallites for the samples calcined at 1000 °C lie in the range from 50 to 253 nm. Additional heat treatment of the samples Ct022 and Ct023 at 1200 °C lead to a minor, but detectable, decrease of the lattice parameters (see Table 2) and to considerable narrowing of the diffraction maxima (Fig. 2). The latest effect is more

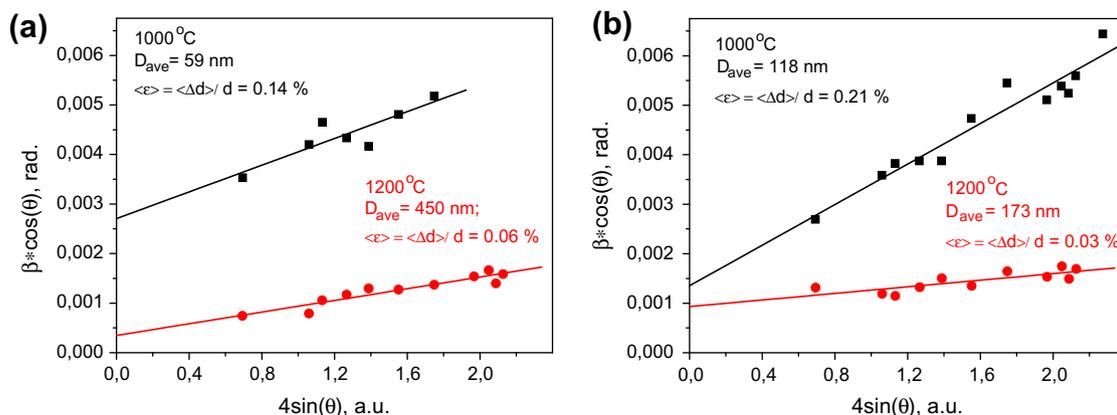


Fig. 3. Graphical results of the Williamson-Hall analysis of microstructure of pure YAG (Ct022, Ct022a) and YAG:Nd (1 mol.%) (Ct023, Ct023a) samples.

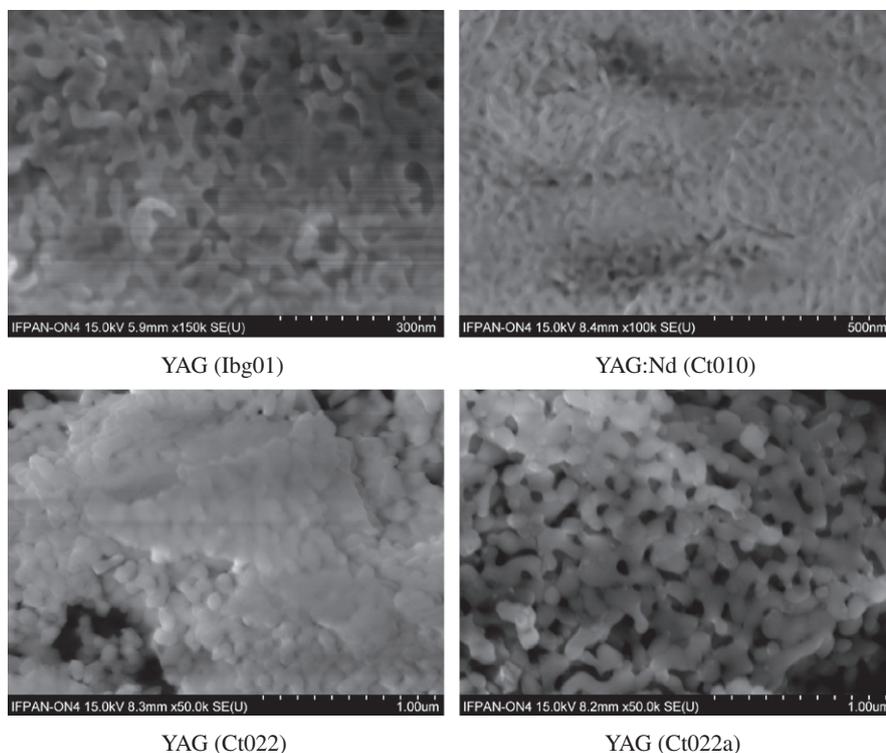


Fig. 4. SEM images of the studied YAG and YAG:Nd powders.

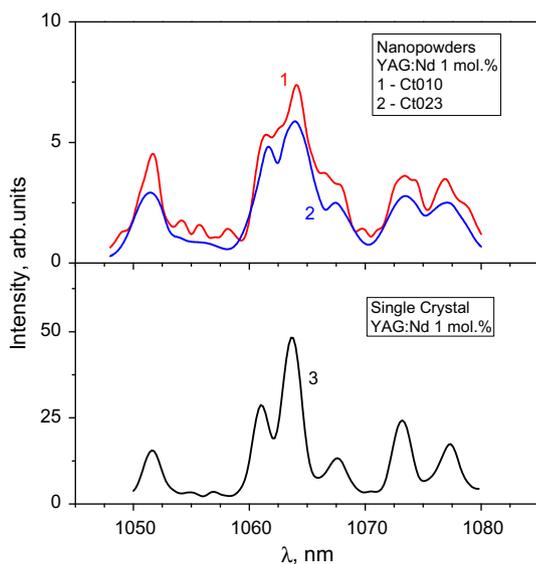


Fig. 5. The photoluminescence spectra of the YAG:Nd (Ct010) (1) and YAG:Nd (Ct023) (2) samples in comparison with a commercially available single crystalline YAG:Nd (1%) (3) recorded at 808 nm laser excitation at room temperature.

pronounced in Ct022a sample, in which drastic increase of crystallite size and noticeable decrease of microstrains are observed. In Ct023a sample, narrowing of diffraction maxima is caused mainly by pronounced decrease of microstrains (in 6–7 times), whereas increase of crystallites size is less pronounced (see Table 2).

The Williamson-Hall plots for the Ct022 and Ct023 samples annealed at two different temperatures are presented in Fig. 3.

The scanning electron microscope studies confirm the crystallites size estimated using the Williamson-Hall method. As it is seen from the images in Fig. 4, the smallest crystallites were observed

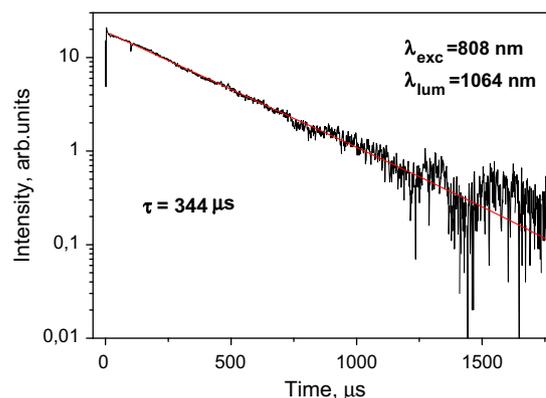


Fig. 6. Decay kinetic of the YAG:Nd (Ct023) sample recorded at 1064 nm using optical excitation at 808 nm at room temperature.

for the pure YAG (Ibg01) sample, whereas the largest ones were observed for the YAG:Nd (Ct022a) sample annealed at 1200 °C.

3.2. Photoluminescent results

The photoluminescence spectra of studied YAG:Nd (Ct010 and Ct023) samples show a characteristic emission of YAG:Nd³⁺ medium in infra-red that corresponds to the ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition in Nd³⁺ ion. The main emission line position is 1064 nm (see Fig. 5). The clear structure of the emission that correlates with the single crystalline medium indicates pure garnet phase for these powder samples.

The decay kinetics measured for Ct023 sample using a pulsed laser excitation at 808 nm reveal a single exponential decay with the lifetime of 344 μs at room temperature (Fig. 6). This value of lifetime is somewhat larger than the decay time of 266 μs measured for single crystalline YAG:Nd (1%) medium. This discrepancy can be

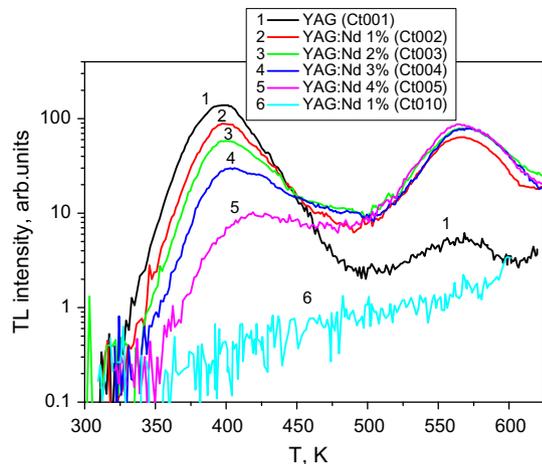


Fig. 7. The thermal glow curves of the studied YAG and YAG:Nd samples after γ -irradiation ($D = 1$ kGy) registered at 800 nm (YAG) and 885 nm (YAG:Nd) at room temperature. Heating rate of 0.4 K/s was used.

caused by energy migration on the grain boundaries of powder samples.

3.3. Thermoluminescent studies

Thermal glow curves of the studied YAG and YAG:Nd samples after γ -irradiation at room temperature are presented in Fig. 7. It

should be noted that a noticeable thermal glow was observed only for the samples from Ct001 to Ct005, which contain parasitic YAM phase. For the rest of samples, like Ct010 in Fig. 7, the glow intensity was too low to be registered.

The glow curves of the Ct001–Ct005 samples have similar structure – a complex peak that consists of two or three peaks at 400–500 K, and a remote peak near 570 K (see Fig. 7). At that, for the nominally pure YAG (Ct001) sample, the peaks at 400–450 K are main ones and the peak at 470 K is a minor one. As for the Nd-doped samples, these peaks are commensurable. Besides, intensity of the peak near 400 K decreases with increasing of neodymium content.

Very similar peaks at 410, 460 and 550 K have been observed before for YAG:Ce and YAG:Ce,Mg single crystals grown by the Czochralski method [8]. The same peaks at 400, 450 and 550 K have been observed by us for polycrystalline YAG:Mn,Si obtained by arc melting technique [9].

According to [10], single crystals of YAG, YAG:Ce and YAG:Ce,Si grown by the Czochralski method from a molybdenum crucible have a main glow peak near 250 °C (~ 520 K) along with few minor peaks below 500 K and above 550 K.

As it was shown in [4], nanocrystalline undoped YAG prepared by a precipitation process reveals thermal glow with main peaks near 200 °C (~ 470 K), 250 °C (~ 520 K) and 300 °C (~ 570 K) or 330 °C (~ 600 K). In the same samples doped with rare-earth ions, similar peaks are observed as well as new high-temperature peaks near 360 °C (630 K) and 400 °C (670 K) appear, namely for YAG:Yb and YAG:Tb [4,5]. Considering the high heating rate (10 °C/s) used

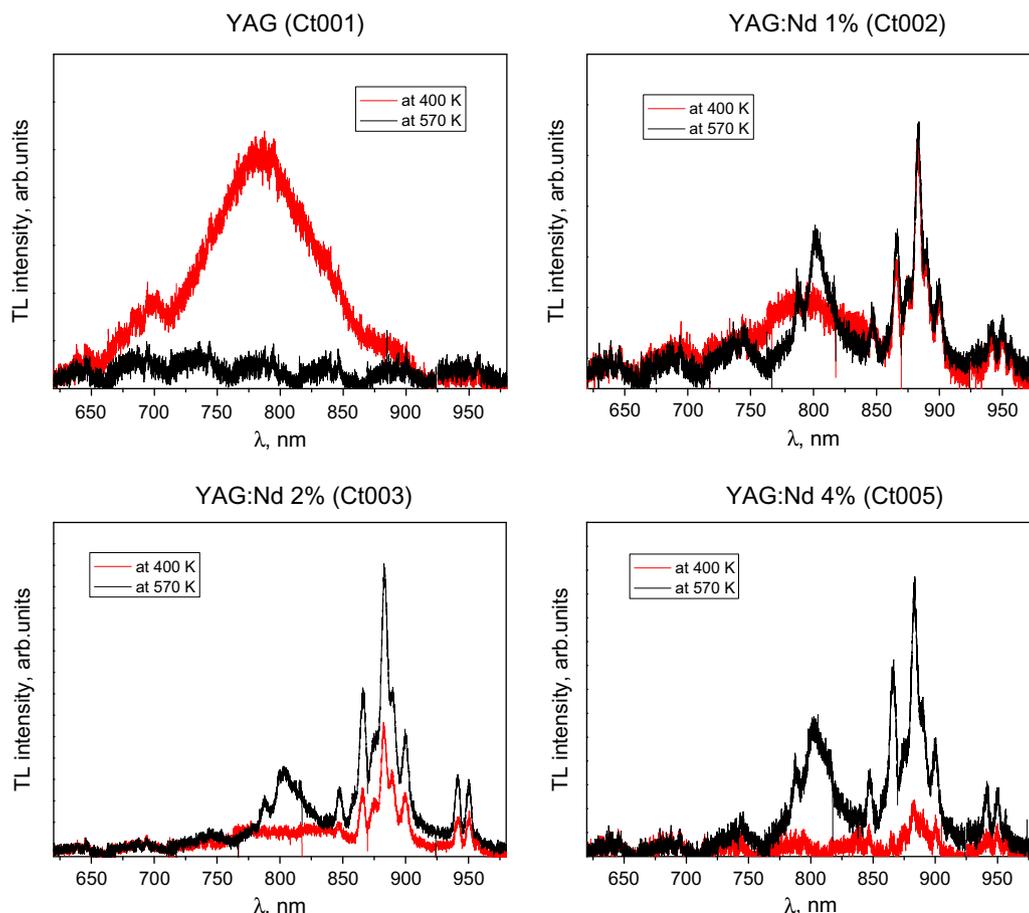


Fig. 8. The thermoluminescence spectra of YAG (Ct001), YAG:Nd (1 mol.%) (Ct002), YAG:Nd (2 mol.%) (Ct003) and YAG:Nd (4 mol.%) (Ct005) samples after γ -irradiation recorded at temperature of 400 K (1) and 570 K (2).

in [4,5], the results presented in these papers are also rather similar to our results.

In such a way the observed here glow peaks near 400, 450 and 570 K we hypothetically consider as typical ones for YAG structure. However, a possible role of YAM (or YAM:Nd) phase cannot be excluded entirely.

The thermoluminescence spectra of the studied samples are shown in Fig. 8. The spectra of nominally pure YAG (Ct001) sample represent a wide emission band around 800 nm that is to all appearance caused by intrinsic defects of YAG or YAM structure. It should be noted that this emission spectrum around 800 nm differ essentially from the thermoluminescence spectrum in blue spectral region reported for the oxygen-deficient YAG crystals [11]. The thermoluminescence spectra of Nd-doped samples represent a superposition of the wide band around 800 nm and a set of narrow lines obviously caused by the $f-f$ transitions of Nd^{3+} ion. At that, the wide-band emission around 800 nm is observed mainly in the glow peaks near 400 and 450 K, and is decreased with increasing of neodymium content. As for the 570 K glow peak, here the Nd^{3+} emission occurs only, so this peak is practically absent in the nominally pure YAG.

As regards the single-phase samples prepared by the technology using citric acid, the absence of thermal glow for these samples testifies their high structure and phase quality. Pure radiation storage properties of this samples is in consistent with the recent results observed for nanocrystalline YAlO_3 (YAP) obtained by similar sol-gel technology [12]. Following the interpretations made in [12], this low-temperature synthesis technology does not allow formation of Y_{Al} antisite ions required for electrons trapping.

Some thermoluminescence observed here only for the “defective” samples, which contain parasitic yttrium-rich YAM phase, corroborate the assumption about the Y_{Al} -related nature of thermoluminescence of both YAP and YAG structures above room temperature. Comparison of the refined values of the YAG lattice parameters for highly stoichiometric YAG samples (Ibg01, Ct022) and the “defective” samples (Ct001) confirms this assumption.

4. Conclusions

A series of nominally pure and Nd-doped YAG nanocrystalline samples were synthesized by sol-gel method using different complexing agents (ethylene glycol and citric acid) and characterized by X-ray powder diffraction, scanning electron microscopy, photoluminescence and thermoluminescence techniques.

Utilization of citrate sol-gel procedure using yttrium and aluminum nitrate nonahydrates as starting substances allowed to obtain highly stoichiometric single-phase YAG and YAG:Nd

nanocrystalline samples with the luminescence performance commensurable with a commercially available single crystalline YAG:Nd.

On the other hand, the obtained material possesses rather poor radiation storage properties to be applicable in thermoluminescence dosimetry that is interpreted by low concentration of the point defects such as Y_{Al} antisite ions or oxygen vacancies.

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