Using silver nanoparticles for the increase of YAG: Ce luminescence

A A Kravtsov\textsuperscript{1,2}, I S Chikulina\textsuperscript{2}, S N Kichuk\textsuperscript{2}, V A Tarala\textsuperscript{2}, M S Nikova\textsuperscript{2} and O V Devitsky\textsuperscript{1,2}

\textsuperscript{1}Laboratory of Physics and Technology of Semiconductor Nanoheterostructures for Microwave Electronics and Photonics, Scientific Group of Technology of Heterostructures, Federal Research Center The Southern Scientific Centre of the Russian Academy of Sciences, 41, Chekhova str., Rostov-on-Don, 344006, Russian Federation

\textsuperscript{2}Faculty of Physics and Technology, North Caucasus Federal University, 1, Pushkina str, Stavropol, 355017, Russian Federation

E-mail: sanya-kravtsov@ya.ru

Abstract. In this study, silver nanoparticles with an average diameter of 50-70 nm were synthesized by the chemical reduction method. Subsequently, nanoparticles in different concentrations were introduced into the YAG: Ce luminescent powder synthesized by the method of two-stage coprecipitation into hexamine. The luminescence of samples with different contents of nanosilver was investigated. It was shown that the direct addition of nanosilver to YAG: Ce significantly impairs luminescence. Upon calcination at 900 °C, an increase in the luminescence of the YAG: Ce samples with silver nanoparticles was observed; however, the luminescence intensity was lower than that of the reference sample (without nanosilver). After calcination in an inert atmosphere at a temperature of 1550 °C, a significant increase in the luminescence intensity (of the order of 30-40 %) of the samples with the addition of a nanosilver was observed in comparison with the reference sample. Thus, silver nanoparticles can be successfully used to improve the YAG: Ce phosphors.

1. Introduction

Today white LEDs are widely used due to their high energy conversion efficiency, durability, and low cost. They successfully replace energy-intensive and inefficient incandescent light bulbs. Although many luminescent materials have been investigated to create white diodes, the most popular yellow phosphor is cerium-doped yttrium aluminum garnet (Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12}: Ce, YAG: Ce). When it is combined with a blue light-emitting chip (such as GaN and InGaN), it gives white emission [1]. This is because YAG: Ce has an intense and wide yellow emission band, which transmits the residual blue color to obtain a white color [2].

YAG: Ce is known as a phosphor for many years. It is widely used for the production of various white light sources such as household and decorative lamps, street spotlights, portable flashlights, etc. However, studies aimed at developing new methods for producing luminescent powders and YAG: Ce ceramics with a higher luminescence efficiency remain relevant [3].
At the same time, it is known that the plasmon effect is a promising way of significantly improving the luminescence intensity by the interaction of emitting centers (for example, rare-earth ions) with plasmon resonance (PR) of noble metals (silver and gold) [4,5]. When the frequency of the exciting beam or the luminescence frequency of rare-earth ions are close to the frequency of the PR band of metal nanoparticles, a strong induced local field can increase the efficiency of the nearby ion luminescence [6]. Co-doping of many phosphors with Ag nanoparticles is being intensively studied as a promising method for enhancing the luminescence of rare-earth ions [7].

In the literature there are no studies dedicated to increasing the YAG: Ce luminescence by doping with silver nanoparticles; therefore, an urgent task is to study the effect of surface plasmon resonance of silver nanoparticles on the luminescence of cerium-doped yttrium-aluminum garnet.

2. Materials and methods

2.1. Methods of synthesis the materials
The silver nanoparticles sol was synthesized by the method of chemical reduction with sodium borohydride [8,9]. The precursor powder was obtained by the method of two-stage precipitation in hexamine [10,11]. Then, the precursor powder was calcined at a temperature of 1150 °C for an hour. The resulting ceramic powder was used for the samples' preparation.

Samples of YAG: Ce luminescent powders with nanosilver were prepared as follows. Different aliquots of nanosilver sol (0.125 ml; 0.25 ml; 0.5 ml; 1 ml) were added to identical weighed portions (2 g) of ceramic powder. Then the resulting mixture was ground with a mortar and pestle and sieved with a 100-mesh screen. Further, the samples were divided into 3 series: the 1st series remained unchanged, the 2nd series of samples was subjected to calcination at 900 °C for 1 hour, the 3rd series of samples was subjected to calcination at 1550 °C in an inert atmosphere for 40 minutes.

2.2. Investigation methods
The size of silver nanoparticles in the sol was estimated by photon correlation spectroscopy on a Photocor Complex instrument. Micrographs of luminescent powders and silver nanoparticles were obtained using a MIRA3-LMH scanning electron microscope with an AZtecEnergy Standard / X-max20 elemental composition determination system. The photoluminescence of the powders was studied using a spectrometric complex assembled on the basis of MDR-23 (LOMO) and MDR-41 (LOMO) monochromators. The phosphor was excited by radiation with a wavelength of λ = 436 nm. The luminescence intensity was measured in the wavelength range of 456-696 nm.

3. Results and discussion
It is known that to exhibit a pronounced effect of plasmon resonance, the silver nanoparticles should not be larger than 200 nm in diameter. In this case, the most pronounced PR effect is observed for particles with a diameter of 10 to 100 nm. Since the size of silver particles is a determining factor, first of all, microscopy and photon correlation spectroscopy of silver nanoparticles was carried out. Figures 1 and 2 show, respectively, an SEM micrograph and a histogram of the distribution of the silver nanoparticles' hydrodynamic radii.

The SEM micrograph was performed in the phase contrast mode (BSE-detector), due to which the silver nanoparticles are visible as white dots. The photograph also shows that the silver nanoparticles are quite densely arranged and have a spherical shape. Agglomeration of particles is not observed due to good stabilization with polyvinylpyrrolidone (PVP). The average particle size according to the SEM results was 50-75 nm. Photon correlation spectroscopy was used to refine the SEM results. The distribution on the histogram is quite wide and close to normal. The maximum of the distribution is located at 25-30 nm, which corresponds to a diameter of 50-60 nm. These values fully support the SEM results. Thus, the nanoparticles obtained in this work satisfy the required dimensions and exhibit the effect of plasmon resonance.
At the next stage, the photoluminescence of YAG: Ce samples with various concentrations of silver nanoparticles was investigated. The luminescence spectra of YAG: Ce powder treated with different amounts of nanosilver sol are shown in figure 3.

It can be seen that a sharp drop in photoluminescence is observed upon the direct addition of nanoparticles to a YAG: Ce ceramic powder. So, the intensity of luminescence decreases almost 2 times when adding only 0.125 ml of nanosilver sol per 2 g of phosphor powder, and about 4 times when adding 0.25 ml. This is explained by the fact that nanosilver has a pronounced absorption band at 350-550 nm. That is, silver nanoparticles mechanically screen particles of the YAG: Ce phosphor powder and absorb those photons that could be spent on the excitation of the phosphor. In this case, silver nanoparticles, despite the PR effect, negatively affect the luminescence, since the positive effect of PR is much less than the negative effect of "screening" of the phosphor by silver nanoparticles.

Thus, to achieve a positive effect, it is necessary to reduce the "screening" effect, while maintaining the silver in the nanoscale state. For this purpose, the previously obtained samples were calcined at 900 °C. The luminescence spectra of YAG: Ce powder treated with various amounts of nanosilver sol after calcination at 900 °C are shown in figure 4. During heat treatment at a given temperature, the polymer-stabilizer of silver nanoparticles (PVP) inevitably burns out. In addition, the oxidation of silver nanoparticles occurs with the formation of an oxide shell. Due to this, the effect of silver nanoparticles' PR is significantly reduced. The spectra of the samples calcined at 900 °C show that the luminescence intensity of the samples with nanosilver increased, but it was still lower than that of the reference sample without nanosilver. This indicates a decrease in the "screening" effect by calcination.

The results suggest that in order to improve the luminescence, the oxidation of nanosilver should not occur, and at the same time, the polymer stabilizing the nanoparticles should burn out. This condition can be met by calcining in an inert atmosphere (for example under coal). In this work, two YAG: Ce samples with nanosilver sol concentrations of 0.125 ml and 0.25 ml were calcined under coal at 1550 °C. The luminescence spectra of the obtained samples are shown in figure 5.
Figure 3. Luminescence spectra of YAG: Ce powder treated with various amounts of nanosilver sol.

Figure 4. Luminescence spectra of YAG: Ce powder treated with various amounts of nanosilver sol after calcination at 900 °C.

Figure 5. Luminescence spectra of YAG: Ce powder treated with different amounts of nanosilver sol after calcination at 1550 °C in an inert atmosphere.

The luminescence intensity of the reference sample (S) increased from 0.02 to 0.025 a. u. This is explained by the growth of YAG: Ce phosphor particles due to diffusion at high temperatures. However, the luminescence intensity of samples S-Ag1(0.125) and S-Ag1(0.25) with silver nanoparticles increased even more, to 0.035 and 0.032 a. u. respectively. Thus, the increase in luminescence was about 30-40%. In this case, an increase in the luminescence intensity was achieved because when YAG: Ce is calcined with silver nanoparticles at 1550 °C in an inert atmosphere, the stabilizer polymer is completely burned out and the silver nanoparticles come into direct contact with the phosphor particles. This enhances the effect of plasmon resonance on luminescence. In addition, the inert atmosphere prevents the oxidation of silver nanoparticles, maintaining the plasmon effect in them.

4. Conclusions
Analyzing the experimental data obtained in this study, we can conclude that nanosilver sol, when it is directly added to YAG: Ce powder, even in a small amount, contributes to a significant decrease in
luminescence. This occurs due to the mechanical screening of active luminescent centers by silver nanoparticles. As a consequence, exciting radiation cannot activate luminescence centers. When the samples were calcined in an inert atmosphere at high temperatures, the stabilizer polymer burned out; however, the silver nanoparticles were not undergone oxidation and retained their properties. As a result, there was a significant increase in the luminescence intensity (by 30–40%) compared to YAG: Ce without silver nanoparticles.

Acknowledgments

This work was supported by the Council for Grants of the President of the Russian Federation (project MK-3786.2021.1.3).

The studies were carried out using the equipment of the Shared Use Center of North-Caucasus Federal University with financial support from the Ministry of Education and Science of Russia, unique project identifier RF ---- 2296.61321X0029 (agreement no. 075-15-2021-687).

References

[1] Nishiura S, Tanabe S, Fujioka K and Fujimoto Y 2011 Properties of transparent Ce:YAG ceramic phosphors for white LED Opt. Mater. (Amst). 33 688-91
[2] Pan Y, Wu M and Su Q 2004 Tailored photoluminescence of YAG:Ce phosphor through various methods J. Phys. Chem. Solids 65 845-50
[3] Yao Q, Zhang L, Zhang J, Jiang Z, Sun B, Shao C, Ma Y, Zhou T, Wang K, Zhang L, Chen H and Wang Y 2019 Simple mass-preparation and enhanced thermal performance of Ce: YAG transparent ceramics for high power white LEDs Ceram. Int. 45 6356-62
[4] Haouari M, Ben Slimen F, Maougi A and Gaumer N 2018 Structural and spectroscopic properties of Eu3+ doped tellurite glass containing silver nanoparticles J. Alloys Compd. 743 586-96
[5] Zhu Y, Wang Y, Zhu J, Zhou D, Qiu D, Xu W, Xu X and Lu Z 2018 Plasmon multiwavelength-sensitized luminescence enhancement of highly transparent Ag/YVO4:Eu3+/PMMA film J. Lumin. 200 158-63
[6] Rajesh D, Amjad R J, Reza Dousti M and de Camargo A S S 2017 Enhanced VIS and NIR emissions of Pr3+ ions in TZYN glasses containing silver ions and nanoparticles J. Alloys Compd. 695 607-12
[7] Malta O L, Santa-Cruz P A, De Sá G F and Auzel F 1985 Fluorescence enhancement induced by the presence of small silver particles in Eu3+ doped materials J. Lumin. 33 261-72
[8] Lunin L S, Lunina M L, Kravtsov A A, Sysoev I A, Blinov A V and Pashchenko A S 2018 Effect of the Ag Nanoparticle Concentration in TiO2–Ag Functional Coatings on the Characteristics of GaInP/GaAs/Ge Photoconverters Semicond 528(52) 993-6
[9] Lunin L S, Devitskii O V, Kravtsov A A and Pashchenko A S 2020 Polymer Films with Silver Nanoparticles Improve the Spectral Characteristics of Photovoltaic Converters Tech. Phys. Lett. 46 98-101
[10] Kravtsov A A, Nikova M S, Vakalov D S, Tarala V A, Chikulina I S, Malyavin F F, Chapuro O M, Krandievsky S O, Kuleshov D S and Lapin V A 2019 Combined effect of MgO sintering additive and stoichiometry deviation on YAG crystal lattice defects Ceram. Int. 45 20178-88
[11] Kravtsov A A, Chikulina I S, Tarala V A, Evtushenko E A, Shama M S, Tarala L V., Malyavin F F, Vakalov D S, Lapin V A and Kuleshov D S 2019 Novel synthesis of low-agglomerated YAG:Yb ceramic nanopowders by two-stage precipitation with the use of hexamine Ceram. Int. 45 1273-82