



Single and multicomponent garnets nanoparticles – Synthesis and luminescence



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ABSTRACT

Luminescent nanopowders of single ($\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$) and multicomponent ($\text{Lu}_2\text{Gd}_1\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$) garnets were synthesized by the solvothermal method in a high pressure autoclave. The synthesis conditions were optimized with respect to morphological and photoluminescence properties. Optimized conditions allow to synthesize well-dispersed nanoparticles with a size of some 30 nm. Concentration quenching of the Ce^{3+} emission as well as luminescence quenching by surface states of nanoparticles were found and discussed.

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1. Introduction

Efficiently emitting luminescent nanoparticles would pave the way for a number of interesting applications, such as emitting layers that can f.e. be used in LEDs or as scintillator. Reasons are that Ce-doped garnet absorb blue light, which is subsequently converted into yellow light. In blue emitting LEDs, this can be exploited to make white light. For application as scintillator, the fast emission (some 60 ns) of the Ce-ion is exploited, together with the fact that garnets are cubic, in this way enabling transparent scintillators without the need for tedious and expensive single crystal growth.

In case of using nanoparticles, the transparency requirement imply well-crystallized nanoparticles with low defect concentrations and with sizes well below 100 nm.

In this work, we selected the solvothermal synthesis in a glycol dispersant (commonly called glycothermal method) out of many methods to synthesize $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ nanoparticles (YAG:Ce NP). Other methods are precipitation [1], sol-gel [2], spray-pyrolysis [3], hydrothermal [4], radiation induced precipitation [5] or combustion [6]. The glycothermal synthesis was discovered by Inoue [7] and first results of this method were reported in the years 1991 – 1995 in [8,9]. The merit of the latter method is that rather low temperatures can be used (we used a temperature of only 225 °C) in the preparation of well-crystallized nanoparticles, preventing uncontrolled particle growth and the formation of agglomerates.

In the glycothermal method, acetates and isopropoxides are used as precursors for the desired composition, f.e. Yttrium acetate hydrate, Cerium acetate hydrate and Aluminium isopropoxide are used in the YAG:Ce synthesis. 1,4-butanediol (BD) is the most frequently used solvent in this synthesis, however other solvents, like 1,3-butanediol [10], a mixture of BD and diethylene glycol (DEG) [11,12], a mixture of BD and polyethylene glycol (PEG) [12] were investigated as well. The synthesis of YAG:Ce NP in 1,3-butanediol leads to formation of crystalline YAG:Ce NP, however under UV excitation, Ce^{3+} luminescence is masked by blue emission from the dispersant [10]. The addition of low amount of DEG (5–15 percent by volume) suppresses aggregation of NP and therefore more stable, transparent and very well dispersed nanoparticles of YAG:Ce are produced [10,11] in comparison to pure BD. This positive effect is likely due to the higher solubility of alumina intermediate states in the solvent mixture. In contrast, the addition of PEG into BD enhances the Ce^{3+} luminescence intensity due to NP surface modification by the passivation of the oxygen vacancies [12]. From both a morphological and luminescence efficiency point of view, the mixture of BD and 5–15 vol% of DEG was found as most promising dispersant for glycothermal synthesis of YAG:Ce nanoparticles. Care has to be taken in adding DEG: it was reported in [10] that increasing the volume fraction of DEG to 20 vol% results in an amorphous and non-luminescent product.

The reaction can be accomplished in a static reactor (a Parr reactor) or stirred autoclave [10,12–15]. The cost and usability of a static reactor outweigh the opportunity of the stirred autoclave. It was found that during the slow reaction at low temperatures in static autoclave, the growth of nanoparticles can be monitored and an intermediate state – alumina layers – can be detected. The

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alumina phase is able to passivate the surface of NP, resulting in an increase of the photoluminescence intensity [10].

The reaction can be performed at low temperature 225–300 °C for different times ranging from 1 h till 5 days. Many variations of aging time and temperature, to optimize the synthesis conditions have been investigated, see e.g. [10,12–15]. It should be mentioned that an additional high temperature firing step is not required to obtain properly crystallized garnet nano-particles [10]. This is confirmed by our investigations, even for multicomponent garnet nano-particles.

Asakura [14] and Pradal [15] have considered the mechanism of the glycothermal reaction and they have assumed a process with three intermediate steps: in step 1 BD and DEG coordinate to the Metal (M) ions and form a glycoxide precursors; in step 2 BD and DEG cyclize and detach to tetrahydrofuran (THF) and 1,4-dioxane, respectively, and M-OH moieties are created; in step 3 M-OH reacts with other Metals (M'-OH) to form M-O-M' bonds, (where M and M' = Al³⁺, Y³⁺ or Ce³⁺).

The addition of citric acid, next to BD, decreases the primary nanoparticle size due to the high efficiency of coordination of carboxyl groups of citric acid to metallic ions on the surface of NP [14]. Citric acid is able to coordinate to the surface to a higher degree than BD and moreover, is able to coordinate in more than one position and is hard to detach from the surface, in consequence suppresses growth of the particles. The efficiency of luminescence of Ce³⁺ increases with increasing amount of the citric acid. However, the phenomenon of the interparticle bridging due the presence of three coordination sites of citric acid is responsible for the negative effect of this solvent, like an aggregation of nanoparticles [14].

The glycothermal reaction can be performed into one- or a two-steps, where nanoparticles prepared by the one-step synthesis are employed as a seed crystals in the two-step glycothermal reaction [12,16]. Generally, second step was consider as a factor which could be responsible for improving morphology of nanoparticles and in the end point, for preventing photobleaching. It was confirmed by the electron loss spectroscopy [12] that photobleaching is attributed to the Ce³⁺ to Ce⁴⁺ ion photo-oxidation near the surface of YAG:Ce NP. The two step synthesis causes the growth of the nanoparticles, however in the same time improves crystallinity and suppress the photobleaching [12].

The glycothermal synthesis does not need additional high temperature firing, as a proper crystal structure has been already obtained during reaction in stirred autoclave at 225 °C [10,15]. However, sometimes 1000–1200 °C firing step in air or reducing atmosphere has been applied, mostly to investigate its influence on the morphology and photoluminescence [13,15,17]. The high temperature heating of as-prepared powders improves particles crystallinity but also results in particle growth, unfortunately. The reported influence of firing on photoluminescence is not consistent. The authors report increasing [15] and decreasing [13] of Ce³⁺ luminescence efficiency after the same heat-treatment and under the same excitation. Our investigations are consistent with results of the second group, where, as-prepared powder has more intense luminescence than fired powder. Such effect is opposite to the conventional one and clearly suggest that organic species on the surface of YAG:Ce NP, which are decomposed by heat-treatment, play a major role to passivate the surface of the luminescent killers and to prevent Ce³⁺ to Ce⁴⁺ oxidation [15].

Researchers [11,15,18] noticed that the glycothermal method has very important engaging features and they line up three: (i) nanoparticles are produced in glycols, which play a role of NP stabilizer and suppress of particles growth and aggregation; (ii) low temperature reaction; and (iii) high dispersion of nanoparticles in the final NP suspension.

Until now, the reports were focused on the single-garnet

compositions like YAG:Ce or Lu₃Al₅O₁₂:Ce (LuAG:Ce) NP. In this paper we present the possibility of using glycothermal reaction in the synthesis of nanoparticles of multicomponent garnet compositions, using Lu₂Gd₁Al₅O₁₂:Ce (LGAG:Ce) as example.

2. Sample synthesis and characterization techniques *Preparation of Y₃Al₅O₁₂:1%Ce (YAG:Ce)*

10 g of Aluminium isopropoxide (stoichiometric amount), 11.336 g of Yttrium acetate hydrate (stoichiometric amount) and 0.111 g of Cerium acetate hydrate were blended with a mixture of solvents: 1,4-butanediol (BD) and diethylene glycol (DEG) in the volume ratio 9:1. The resulting colloidal solution was stirred on a hot plate for 3 h while mildly heating of 50 °C. Then, the additional stirring step with a ultra-high speed homogenizer IKA Ultra Turrax was applied to obtain a smooth and very well homogenized suspension. This suspension was poured into the 500 ml High Pressure Reactor P-Line from Premex and constantly stirred (300 rpm) and heated at 225 °C for 60 h. The reaction temperature was reached by applying a heating rate of 1.5 °C/min. Before the process was started, the undesired air present in the autoclave was flushed away with Argon. The inner pressure reached around 50 bars after 2.5 h. At the end of the process the mixture was cooled down and a stable, translucent yellowish suspension was obtained. The organic by-products like 1,4-dioxane and tetrahydrofuran and dispersants (BD and DEG) were removed by high speed centrifugation (10 000 rpm) and drying at 120 °C in a vacuum oven. An additional firing step is not needed to get a proper garnet structure. However, an additional firing step at 1200 °C in air has been performed for a few samples and will be discussed only for comparison.

The parameters of synthesis conditions and compositions such as: synthesis time (from 10 till 120 h), ratio of BD and DEG (from 100 till 90% of BD), amount of Aluminium isopropoxide or Yttrium acetate hydrate (stoichiometric and 15% excess of Y³⁺ or Al³⁺) and Ce³⁺ concentration (from 0.4 till 3%) were checked and optimized for morphology and efficiency of photoluminescence. The synthesis conditions were optimized for YAG:Ce and the parameters obtained were also used in the Lu₂Gd₁Al₅O₁₂:1%Ce (LGAG:Ce) nanoparticles synthesis.

The most frequently used parameters are: 60 h aging time, 9 BD:1 DEG, stoichiometric amount of Y and Al-precursors, 1% Ce; all changes were marked in the captions or in the text.

2.1. Preparation of Lu₂Gd₁Al₅O₁₂:1%Ce (LGAG:Ce)

10 g of Aluminium isopropoxide, 11.2939 g of Lutetium acetate hydrate (slightly less than the stoichiometric amount), 3.7646 g of Gadolinium acetate hydrate and 0.1027 g of Cerium acetate hydrate were blended, homogenized and heated together with a mixture of BD and DEG with the same procedure like for YAG:Ce (see above). The optimal parameters of heating in the autoclave were adjusted: 225 °C for 60 h with a linear heating rate of 1.5 °C/min.

2.2. Structural and morphological characterization

The phase purity of the synthesized powders was checked by powder X-ray diffraction (XRD) on a Panalytical X'Pert Pro MPD diffractometer equipped with a Cu K α X-ray source and X'Celerator detector.

The electron micrographs were recorded with a FEI Nova600 NanoSEM (Scanning Electron Microscope) system using secondary electrons. The powders were dispersed in isopropyl alcohol (IPA) using a Branson Ultrasonics and perched on the Silicon Wafer. The

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