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Garnet-Type Nanophosphors for White LED Lighting

Alexandra Cantarano[†], *Alain Ibanez*[†] *and Géraldine Dantelle*[*†]

Univ. Grenoble Alpes, CNRS, Grenoble INP, Institut Néel, Grenoble, France

In this article we present a short review of the main wet chemical methods developed for the preparation of Ce^{3+}-doped $Y_3Al_5O_{12}$ (YAG:Ce) nanocrystals for their use as nanophosphors in LED lighting technology: combustion, co-precipitation, sol-gel, modified-Péchini, and solvothermal routes. We highlight the key synthesis steps and discuss them in the view of the size, crystal quality, and agglomeration state of the obtained nanocrystals. The photoluminescence internal quantum yield of these nanocrystals is also discussed in light of their morphology. In addition, we report on other garnet-type nanophosphors [$Gd_3Sc_2Al_3O_{12}$, $(Gd,Y)_3Al_5O_{12}$, etc.] doped with lanthanide ions (Ce^{3+}, but also Eu^{3+} or Dy^{3+}) developed with the goal of obtaining a warmer white light. The spectroscopic properties of these nanophosphors, in particular their emission range, is discussed in relation with the doping nature, doping concentration, and crystal field of the host matrices.

Keywords: nanocrystals, YAG:Ce, garnet, photoluminescence, LED lighting

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***Correspondence:**
Géraldine Dantelle
geraldine.dantelle@neel.cnrs.fr

[†]*These authors have contributed equally to this work*

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INTRODUCTION

The advent of semiconductor technology has led to significant advances in lighting devices with the commercialization of white Light Emitting Diodes (wLEDs). Previously relegated to colored light applications, LEDs now successfully compete with conventional technologies in various general lighting applications and are leading products for the automotive market, for example. They are generally based on a GaN/InGaN chip, emitting in the blue, around 450 nm, coupled with a micron-sized luminescent garnet phosphor ($Y_3Al_5O_{12}$ doped with Ce^{3+}, YAG:Ce) (Nakamura and Fasol, 1997). This phosphor powder, encapsulated in an epoxy or silicone resin, is placed above the chip (remote phosphor) and partially absorbs the blue light to down-convert in the yellow range thus leading to white light emissions. However, the micron-size of YAG:Ce phosphors induces several drawbacks: (1) backscattering toward the blue chip, both reducing the external efficiency of the wLEDs at around 60% and damaging gradually the chip, thus reducing the device lifetime (Narendran et al., 2005); (2) need to encapsulate the phosphors in a resin to obtain a mechanically stable layer, the binder leading to accelerated aging of the wLEDs (Yang et al., 2012; Hang et al., 2013); (3) poor coupling with blue nanostructured chips that are now emerging, such as InGaN nanowire arrays for micro-displays (Ley et al., 2019). Moreover, with regard to the latter point in particular, the use of micron-sized phosphors is unsuitable to implement additive manufacturing techniques, which are quickly rising as a potential benefit to wLED developments. Indeed, the performance of modern LED devices can indeed be significantly improved by 2D and 3D printing, particularly by specially designed nano/micro-structures within LEDs requiring, which needs nanophosphors. Thus, to overcome these drawbacks, the use of nanophosphors with particle sizes smaller than 100 nm is required: (1) to control light scattering and enhance the light extraction that is directly associated with the emission efficiency of wLEDs devices; (2) to

perform the phosphor shaping without any binder, as also targeted by researchers working on glass-ceramic phosphors (Chen et al., 2015), and to obtain a better coupling with nanostructured semi-conducting heterostructures (Schimpke et al., 2016); (3) to deposit phosphor layers by 2D and 3D printing on nanostructured diodes by ink-jet techniques, involving phosphor nanocrystals (NCs with diameter <100 nm) dispersed in solution with very good colloidal stability (Zhan et al., 2017). Another problem with the YAG:Ce phosphors, that is unrelated to particle size, is their yellow emission, leading to wLEDs exhibiting poor color rendering indexes (CRI), characterized by a cold white emission, uncomfortable for human eyes.

In this article, we review different chemical methods for the preparation of YAG:Ce NCs, pointing out their size and crystal quality, their aggregation or agglomeration state (Nichols et al., 2002) and finally their internal luminescence quantum yield (iQY). We then focus on other garnet-type nanophosphors whose spectroscopic properties are more appropriate to elaborate warm white LED lighting.

SYNTHESIS OF YAG:CE NANOCRYSTALS

Solid-state reaction, used to synthesize commercial YAG:Ce powder, requires high temperature treatment (>1,500°C), which is energy-consuming and leads to micron-sized phosphors with an iQY of 87% (Xu et al., 2009; George et al., 2013b; Song et al., 2013). To synthesize YAG:Ce NCs, several approaches can be envisioned: (1) a top-down strategy, consisting in intensive grinding of micron-sized powder, but it induces a large number of surface defects acting as luminescence quencher; (2) bottom-up approaches, including Chemical Vapor Deposition (Murai et al., 2016), Pulsed Laser Deposition (Dejene, 2016), or wet chemical routes, such as combustion (Hess et al., 1994; Shi and Wang, 2001; Upasani et al., 2019), co-precipitation (Chen et al., 1999; Chiang et al., 2006; Kumar and Senthilselvan, 2017), sol-gel (Kareiva, 2011; Boukerika et al., 2014), modified Péchini (Belyakov and Kulikov, 2011), and solvothermal (Inoue et al., 1991; Nyman et al., 2009; Dantelle et al., 2018a) routes. In the following, we will detail the main wet chemical routes, which present the advantage of being cheaper than the others. Moreover, these wet chemical processes allow to achieve balanced mixture of precursors at the molecular level, resulting in the lowering of the nanoYAG crystallization temperature.

COMBUSTION SYNTHESES

This YAG:Ce NC synthesis route consists in an exothermic reaction between a fuel, typically urea or glycine as reducing agent, and yttrium, aluminum, and cerium nitrates as oxidizers (Fu et al., 2008; Gupta et al., 2011; Wu et al., 2016). The combustion is initiated by an external heating (∼500°C) followed by a high temperature treatment around 1,000°C to yield pure YAG and improve the Ce^{3+} incorporation into the matrix (Shi and Wang, 2001; Yang et al., 2006; Sawala et al., 2016). The combustion step leads to large and irregular particles containing lots of pores because of the gases liberated during the fuel combustion, while the high-temperature treatment required to crystallize the YAG phase results in strong particle sintering, which leads to highly agglomerated NCs (Shi and Wang, 2001; Abd et al., 2018). An alternative consists in mixing yttrium nitrate with glycine and aluminum nitrate with urea to avoid a subsequent heat treatment and reduce the NC agglomeration (Gupta et al., 2011; Dhadade et al., 2016; Sawala et al., 2016). It led to 40 nm particles agglomerated in 100–200 nm clusters, presenting an iQY of 54% (Haranath et al., 2006). The main issue of the combustion technique is the temperature inhomogeneity through the reacting mixture with the occurrence of the so-called "hot spots." This leads to inhomogeneities in chemical composition with the formation of spurious phases such as $YAlO_3$ and $Y_4Al_2O_9$ (Hess et al., 1994; Yang et al., 2006), but also inhomogeneities in particle morphology with a broad size distribution. This is due to heterogeneous nucleation, growth and coalescence mechanisms, which are enhanced by the further high temperature treatment. In 2017, Abd et al. managed to synthesize YAG:Ce NCs through a shortened combustion synthesis, thanks to laser-assisted or microwave-assisted reaction (Abd et al., 2017, 2018). This latter yielded well-crystallized YAG:Ce NCs of about 60 nm in one-step with reduced, but still present, NC agglomeration (**Figure 1A**; Abd et al., 2019). To conclude, the combustion synthesis is a rapid and simple process requiring high temperature treatment to obtain crystalline NCs with high luminescence intensity, but with a severe agglomeration.

CO-PRECIPITATION METHODS

Chemical precipitation syntheses of YAG:Ce NCs have been commonly used by the normal strike technique or by the reverse strike route through the pH control of aqueous solutions. For normal strike, a basic solution (ammonium bicarbonate, ammonium hydroxide, etc., as precipitants) is added into an acidic one (nitrate precursor solution) or the other way around (reverse strike) (Yuan and Ryu, 2004; Caponetti et al., 2005; Zhang et al., 2008). Other routes used alcohol-water as precipitant solvent, the alcohol acting also as surfactant reducing initial NC aggregation (Tong et al., 2007). The obtained precipitate (hydroxides, carbonates, hydroxycarbonates…) requires a subsequent calcination at a temperature superior to 1,000°C to obtain pure nanoYAG with moderate to severe agglomeration and wide size dispersion: from a few hundreds of nanometers to micrometer NC agglomerates (Wang et al., 2016; Qiu et al., 2017; Tian et al., 2020). To tackle these issues, Qiu et al. showed that acidic conditions led to smaller YAG:Ce crystal size since it fosters the precipitation of Al^{3+} (aggregation of 65 nm crystals) and narrow size dispersion, alongside with higher emission intensity (Qiu et al., 2017). To reduce even more the agglomeration of YAG:Ce NCs, surfactants, such as steric stabilizers (polyethylene glycol, PEG10000), electric stabilizers [$(NH_4)_2SO_4$, $C_{12}H_{25}SO_4Na$], or other dispersing agents (e.g., graphene oxide nanosheets) (Li and Wang, 2009; Wang et al., 2009; Zhang and Yu, 2009; Que et al., 2017; Ji et al., 2018)

were involved in the initial solutions, resulting after ∼1,000°C calcination in nanoYAG (about 70 nm) with narrow particle size distribution, spherical shapes, moderate NC agglomeration, and enhanced PL emission intensity. With no surfactant but by combining ultrasonication during the addition of the initial solution to the precipitant and microwave heating, Si et al. managed to produce uniformly dispersed 18 nm (900°C) to 43 nm (1,100°C, **Figure 1B**) YAG particles depending on the annealing temperature, with reduced agglomeration (Si et al., 2014). Very recently, Gaiser et al. published an original two-step approach, including first the formation of particles in ionic liquid solution, followed by a heat-treatment at 600°C to crystallize YAG:Ce NCs embedded in a LiCl matrix, preventing their agglomeration. This process results in individual NCs with an average size below 100 nm, presenting a iQY of 51% (Gaiser et al., 2019).

Hence, the co-precipitation method allows the production of YAG:Ce NCs with relatively narrow size distribution. However, a high temperature calcination step is still required to either yield pure YAG phase and to improve emission properties, favoring agglomerated NCs if no care is taken.

SOL-GEL ROUTE AND MODIFIED PÉCHINI METHOD

The sol-gel synthesis of YAG:Ce NCs involves metal alkoxides as Y, Al precursors (which can be partly replaced by metal salts, generally Y or Ce nitrates) in alcoholic or aqueous solutions, that are converted into a gel through hydrolysis and condensation reactions (∼60°C) (Veith et al., 1999; Devi et al., 2008; Boukerika et al., 2014; Zhang et al., 2017). The resulting gels are then dried into powders and further annealed at around 1,000°C, leading to YAG NCs with different agglomeration levels depending on temperature, duration and atmosphere used during heating treatments (Kareiva, 2011; Boukerika et al., 2016; Sundarakannan and Kottaisamy, 2016). Several conditions have been implemented to have a better control over the YAG:Ce particle size. In 2018, Singlard et al. managed to control the YAG:Ce NC size from 55 to 123 nm with metal concentration variation (Singlard et al., 2018). There are only few papers reporting iQY values for the sol-gel prepared YAG:Ce NCs. Murai et al. reported a thin YAG:Ce film formed of coalesced particles with a iQY of 65% via an epoxide-catalyzed sol-gel method with a 1,600°C heating treatment (Murai et al., 2012).

An important drawback of the sol-gel route is due to the high reactivity of the alkoxides precursors, with the risk of significant metal inhomogeneity in the gel. Thus, the modified Péchini method was used as an alternative to overcome the sol-gel route limitations, particularly to improve the control of YAG:Ce NC size. In the modified Péchini method, the metal ions are first chelated in aqueous solutions, usually by citric acid, which reacts then with a polyalcohol (typically ethylene glycol) giving viscous resins, through poly-esterification reactions, where metal ions are highly dispersed. After an annealing step, it leads to a lowered size of 50–70 nm NCs with agglomerates up to a few hundreds of nanometers (**Figure 1C** for a sample annealed at 1,030°C) (Zych et al., 2008; Zhang et al., 2009; Hassanzadeh-Tabrizi, 2012; He et al., 2016). Mamonova et al. synthesized freely dispersed individuals NCs of about 100 nm with increased emission intensity through an additional annealing in molten salts (Mamonova et al., 2017).

Although the sol-gel route involves low cost products and is broadly developed to synthesize rare-earth doped metal oxides (Danks et al., 2016), it is a complex method requiring control over a large number of parameters: pH, temperature, annealing parameters, reactant concentration, additives, complexing agent. It leads to poor control on the YAG:Ce NC size and do not allow to get YAG NC dispersion in a solvent, an essential step for further nanophosphor shaping. The modified Péchini method, a simpler alternative to sol-gel route allowing a deeper control over the NCs size, nevertheless requires high temperature treatments, favoring NC coalescence, and agglomeration, which are not usually sufficient to remove all the organic residues (Belyakov and Kulikov, 2011).

SOLVOTHERMAL METHOD

The conventional solvothermal route consists in heating in an autoclave (up to 300°C) a precursor solution composed of yttrium and cerium acetates, aluminum isopropoxide, and 1.4-butanediol used as solvent. An autogenous pressure builds inside the autoclave up to about 60 bars in a few hours (Kasuya et al., 2006; Kamiyama et al., 2010; Ramanujam et al., 2016). The combination of pressure and temperature leads to non-equilibrium conditions, allowing the nanocrystallization of YAG:Ce NCs, without any subsequent thermal treatment of nanopowders. This represents an important advantage to avoid NC coalescence and agglomeration that inevitably occur during the final high temperature treatments required for the previous synthesis routes. Depending on the reaction time and temperature, the conventional solvothermal method commonly yields YAG:Ce particles from 20 to 100 nm (Kasuya et al., 2005; Isobe, 2006; Nyman et al., 2009; Vorsthove and Kynast, 2011). These particles are usually composed of spherical NCs of a few nanometers with the formation of large cauliflower-shape agglomerates (**Figure 1D**; Kasuya et al., 2005) exhibiting PL iQY between 20 and 30% (Kasuya et al., 2005; Asakura et al., 2006; Nyman et al., 2009).

To improve the crystal quality and, subsequently the iQY of YAG:Ce NCs, Revaux et al. proposed a protected annealing method consisting in annealing at 1,000°C YAG:Ce NCs previously dispersed in a porous silica, which preserves their nanometer size of YAG:Ce (Revaux et al., 2011). This method led to 60 nm highly crystalline and well-dispersed NCs with an iQY of 60%. However, to retrieve the NCs, silica should be dissolved by hydrofluoric acid, highly toxic, which is not appropriate for any industrial development. In 2017, Odziomek et al. managed to synthesize ultra-small individual and monodispersed YAG:Ce NCs (4–5 nm) (**Figure 1E**) by dehydrating the starting precursors and adding diethylene

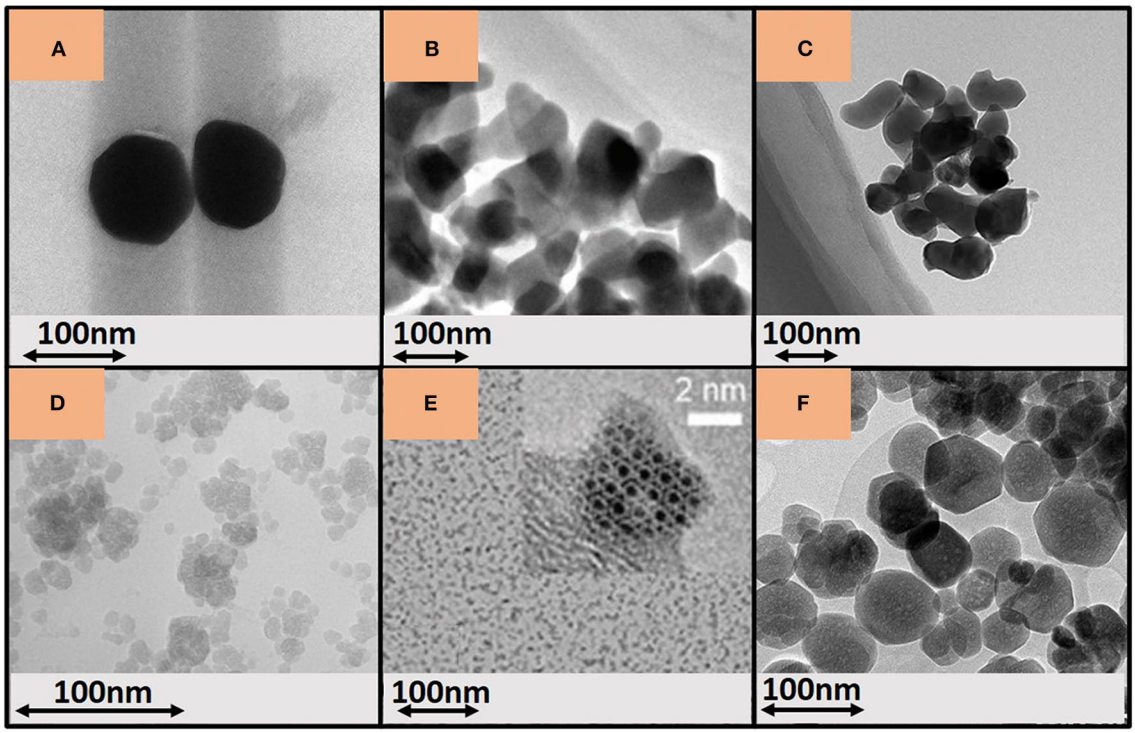

FIGURE 1 | Microscopy images of YAG:Ce NCs prepared **(A)** by combustion, reproduced from Abd et al. (2019), with permission from the authors; **(B)** by co-precipitation, reproduced from Si et al. (2014), under the Creative Commons CC BY license; **(C)** by modified Péchini method, reproduced from He (2016), under the Creative Commons CC BY license; **(D)** by conventional solvothermal synthesis. Image reproduced from Kasuya et al. (2005), with permission from American Chemical Society, Copyright (2020); **(E)** by solvothermal synthesis after precursor dehydration and adding diethylene glycol. Image reproduced from Odziomek et al. (2017), with permission from The Royal Society of Chemistry; **(F)** by modified solvothermal synthesis, high pressure, and steady high temperature. Image reproduced from Dantelle et al. (2018a), under the Creative Commons CC BY license.

glycol (Odziomek et al., 2017). The addition of a co-solvent contributes to size reduction and minimized NC aggregation. Recently, Dantelle et al. introduced a modified solvothermal process by combining high temperature (400°C) and steady high pressure (200 bar) to produce well-crystallized individuals YAG:Ce NCs with iQY of 40% (**Figure 1F**; Dantelle et al., 2018a).

The solvothermal method, scalable, and relatively cheap, appears as a highly promising route to synthesize highly crystalline YAG:Ce NCs that can be dispersed in ethanol without aggregation, opening the route to NC deposition through ink-jet printing and to the formation of 2D and 3D phosphor layers for white LED nanostructured devices.

NEW NANOPHOSPHORS FOR WHITE LED LIGHTING

Although YAG:Ce nanophosphors have been at the center of attention for the development of nanostructured LED lighting, other garnet-type nanophosphors are developed, using the synthesis methods presented above. Indeed, the combination of YAG:Ce and InGaN blue diode leads to a so-called "cold white" LED lighting, which can be responsible for eye discomfort and even, at high power, for retina damage (Behar-Cohen et al., 2011). A great amount of work has been made to propose phosphors, at the micron scale, that would present a red-shifted emission, leading to a warmer white light (George et al., 2013a; Li et al., 2015). Due to its stable chemical and optical properties, garnet-type structure provides excellent hosts, able to incorporate various lanthanide and transition metal ions (Setlur et al., 2008; Xia and Meijerink, 2017; Wang et al., 2019). Two strategies have been followed: (1) The first one consists in synthesizing new Ce^{3+}-doped garnet compounds whose emission is shifted due to the crystal field effect of the host matrix. Indeed, Ce^{3+} emission is based on the radiative de-excitation from 5d levels, sensitive to the local environment, to 4f levels, and thus varies with the host nature; (2) The second strategy consists in modifying the nature of the doping ions and incorporating other lanthanide or transition metal ions whose electronic transitions fall in the red range.

With the need for miniaturization and better coupling with nanostructured diodes, the search for new nanophosphors with a redder emission has been launched (Cesaria and Di Bartolo, 2019), with the challenge to control the phase purity of these new compounds, as well as their NC size and crystal quality to obtain high PL efficiency.

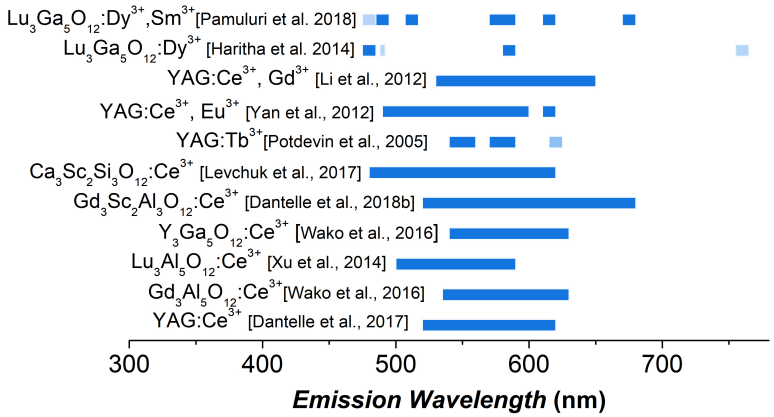

FIGURE 2 | Emission range of different garnet-type nanophosphors reported in the literature. The emission range has been defined by considering all emission whose intensity is larger than Imax/2, with Imax the maximal PL emission intensity. The dark blue indicates a strong emission intensity, in comparison to the light blue. No emission intensity comparison can be done among the different nanophosphors.

NEW GARNET-TYPE NANOPHOSPHORS DOPED WITH CE^{3+}

According to Wu et al. (2007), and more recently to Ueda and Tanabe (Ueda and Tanabe, 2019), the emission wavelength of Ce^{3+} is directly related to the distortion of the dodecahedral site occupied by Ce^{3+}, in the different garnet structures. Through thorough studies at the micron scale, it was shown that the bigger the site distortion, the more red-shifted the emission. Based on the numerous studies at the micron-sized level, several garnet-type nanophosphors have been developed. As shown on **Figure 2**, for nanophosphors, the substitution of Y^{3+} by Gd^{3+} ($r_{Y^{3+}} = 1.019$ Å vs. $r_{Gd^{3+}} = 1.053$ Å, coordination number, CN = 8) induces a red-shift of the emission of about 10 nm (Wako et al., 2016; Dantelle et al., 2017), whereas the Y^{3+} substitution by Lu^{3+} ($r_{Lu^{3+}} = 0.977$ Å) shifts the emission toward the blue region (Praveena et al., 2011; Xu et al., 2014). Meanwhile, the substitution of octahedral aluminum ($r_{Al^{3+}} = 0.535$ Å, CN = 6) by Ga^{3+} ($r_{Ga^{3+}} = 0.66$ Å, CN = 6) induces a 10 nm blue-shift of the emission (Dantelle et al., 2017) and, in $Gd_3Sc_2Al_3O_{12}:Ce^{3+}$ NCs doped with 10 mol.% Ce^{3+}, a significant red-shift of about 50 nm is observed (Dantelle et al., 2018b). These nanoscale evolutions follow the trends obtained at the micron scale and can be explained by the influence of the host crystal field, leading to different splittings of the 5d levels of Ce^{3+} responsible for the emission. Other garnets, such as Ce^{3+}-doped silicate garnet $Ca_3Sc_2Si_3O_{12}$ (Levchuk et al., 2017), can be good alternatives to provide red emission. Note that, at present time, most of the garnet-type nanophosphor work reported in the literature deal with strongly agglomerate particles synthesized mainly by the sol-gel method, which is not entirely satisfactory for the use of NCs in nanostructured white LED lighting.

Interestingly, as the synthesis methods employed to elaborate NCs involve non-equilibrium conditions, YAG:Ce NCs can be doped with higher concentration than their bulk equivalent. Thus, up to 13 mol.% Ce was introduced in YAG NCs produced by low-energy cluster beam deposition (Masenelli et al., 2013), and up to 30 mol.% using auto-combustion method (Haranath et al., 2006). Although the maximal quantum efficiency is usually obtained for a low doping concentration, high doping could allow to redshift the emission. Indeed, in Ce^{3+}-doped YAG and $Gd_3Sc_2Al_3O_{12}$, emission is redshifted by increasing the cerium concentration from 1 mol. to 10 mol.% (Masenelli et al., 2013; Devys et al., 2017). This phenomenon can be an advantage for tuning the emission wavelength while using garnet-type nanophosphors and is explained by the fact that Ce^{3+} ions ($r_{Ce3+} = 1.143$ Å) substitutes Y^{3+}, inducing more distortion within the crystal lattice.

GARNET-TYPE NANOPHOSPHORS DOPED WITH OTHER LN^{3+} IONS

The second strategy to obtain phosphors with a redshifted emission consists in introducing other doping ions than Ce^{3+}: other trivalent lanthanide ions, divalent lanthanide ions or transition metal ions. A large number of papers, dealing with garnets at the micron scale, report such doping modifications (Shang et al., 2014; Xia and Meijerink, 2017; Wang et al., 2019). At the nanoscale, the literature is scarcer and mainly reports nanophosphors doped with trivalent lanthanide ions (Gd^{3+}, Eu^{3+}, Sm^{3+}, Dy^{3+}, Tb^{3+}), exhibiting electronic intra-configurational transitions in the red range. Such ions are incorporated as dopant or co-dopant in the garnet-type nanophosphors and provide red emission components (**Figure 2**; Potdevin et al., 2005; Li and Shen, 2012; Yan et al., 2012; Haritha et al., 2014; Pamuluri et al., 2018; Ali and Khedr, 2019).

The utility of these nanophosphors for wLED lighting can be evaluated by the calculation of their color coordinates (x,y), the correlated color temperature (CCT) and the color rendering index (CRI). The standard illuminant, corresponding

to the average daylight, presents color coordinates of (0.31,0.33) and a CCT around 6,500 K (Noboru and Robertson, 2005). YAG:Ce-based wLEDs, give CCT values higher than 7,000 K ("cold white") and a maximal CRI of ∼80, according to Ce^{3+} concentration and phosphor thickness (Hua et al., 2016). Thanks to their red emission component, the above-mentioned compounds can be combined to semi-conducting diodes and provide better CCT and CRI. For instance, an optimized wLED combining YAG:Ce and YAG:Ce,Gd nanophosphors with a InGaN chip exhibits color coordinates of (0.31,0.32), a CCT of 6,564 K and a CRI of 86 (Li and Shen, 2012). Another example is Dy^{3+}-doped $Lu_3Al_5O_{12}$ nanophosphors, showing interesting color coordinates (0.317,0.321) and a CCT of 6,322 K, close to the ideal white light (Pamuluri et al., 2018).

In comparison to micron-sized phosphors, additional challenges appear when working with nanophosphors due to the crystal size and the synthesis methods involved. Indeed, if the Ln^{3+} emission wavelength is not affected by the size reduction, the PL efficiency and energy transfer between doping ions can be different due to surface traps and volume defects (Dantelle et al., 2018a; Liu et al., 2018). Moreover, the control of the oxidation state at the nanoscale is problematic. Indeed, when working with micron-sized powder, typical annealing under controlled atmosphere can be performed to stabilize the oxidation state of the doping ion, as for Ce^{3+}-doped YAG (George et al., 2013b) and also in Eu^{2+}-doped YAG (Havlák et al., 2016). To obtain NCs, post-annealing should be avoided, making the control of the oxidation state more complex. For instance, when using solvothermal method, Dantelle et al. showed by X-ray absorption spectroscopy that a non-negligible fraction of cerium ions (nearly 50%, depending on the synthesis temperature) were oxidized (Dantelle et al., 2018a). To preserve the right oxidation state while elaborating NCs, more complex strategies should be proposed. A recent study proposes the bubbling of a reducing gas in a solution prior to solvothermal treatment, preventing partially the oxidation of Ce^{3+} during the heat treatment (Cantarano et al., 2020).

CONCLUSION

Several solution-based methods (co-precipitation, sol-gel, solvothermal, etc.) have been developed for the synthesis of YAG:Ce NCs. However, most of them involve an annealing step at high temperature (typically above 800°C), which induces NC agglomeration and thus prevents their dispersion in solution and their further deposition onto blue LEDs. The solvothermal method, occurring completely in solution and requiring no further annealing, appears as an efficient way to produce non-agglomerated NCs. However, many parameters (pressure, temperature, solvent, etc.) should be controlled to control YAG:Ce nanocrystallization and to produce highly luminescent NCs. Aside the YAG:Ce nanophosphor, other garnet-type nanophosphors are developed with the goal of obtaining a red-shift emission. This emission shift can be obtained by considering either another garnet-type matrix or other doping ions, on the model of works performing at the micron scale. However, each new compound requires thorough nanocrystallization study to control the size, morphology, and PL properties. Hence, the synthesis of nanophosphors for white LED lighting still remains a real challenge. Perspectives also include nanophosphor shaping, using low cost techniques based on solution such as inkjet printing onto semi-conducting chips. The development of such wLED devices should allow better control of light scattering, minimization of optical losses, better coupling with nanostructured blue diodes for enhanced efficiency and miniaturization of the devices.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct and intellectual contribution to the work, and approved it for publication.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.