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1 Garnet-type nanophosphors for white LED lighting

2 Alexandra Cantarano¹, Alain Ibanez¹, Géraldine Dantelle^{1,*}

3 ¹Univ. Grenoble Alpes, CNRS, Grenoble INP, Institut Néel, 38000 Grenoble, France

4 * Correspondence:

5 Corresponding Author

6 geraldine.dantelle@neel.cnrs.fr

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

8

9 Abstract

10 In this article we present a short review of the main wet chemical methods developed for the preparation
11 of Ce³⁺-doped Y₃Al₅O₁₂ (YAG:Ce) nanocrystals for their use as nanophosphors in LED lighting
12 technology : combustion, co-precipitation, sol-gel, modified-Péchine and solvothermal routes. We
13 highlight the key synthesis steps and discuss them in the view of the size, crystal quality and
14 agglomeration state of the obtained nanocrystals. The photoluminescence internal quantum yield of
15 these nanocrystals is also discussed in light of their morphology. In addition, we report on other garnet-
16 type nanophosphors (Gd₃Sc₂Al₃O₁₂, (Gd,Y)₃Al₅O₁₂, etc) doped with lanthanide ions (Ce³⁺, but also
17 Eu³⁺ or Dy³⁺) developed with the goal of obtaining a warmer white light. The spectroscopic properties
18 of these nanophosphors, in particular their emission range, is discussed in relation with the doping
19 nature, doping concentration and crystal field of the host matrices.

20

21

22 1 Introduction

23 The advent of semiconductor technology has led to significant advances in lighting devices with the
24 commercialization of white Light Emitting Diodes (wLEDs). Previously relegated to colored light
25 applications, LEDs now successfully compete with conventional technologies in various general
26 lighting applications and are leading products for the automotive market, for example. They are
27 generally based on a GaN/InGaN chip, emitting in the blue, around 450 nm, coupled with a micron-
28 sized luminescent garnet phosphor (Y₃Al₅O₁₂ doped with Ce³⁺, YAG:Ce) [1]. This phosphor powder,
29 encapsulated in an epoxy or silicone resin, is placed above the chip (remote phosphor) and partially
30 absorbs the blue light to down-convert in the yellow range thus leading to white light emissions.
31 However, the micron-size of YAG:Ce phosphors induces several drawbacks: (1) backscattering
32 towards the blue chip, both reducing the external efficiency of the wLEDs at around 60 % and
33 damaging gradually the chip, thus reducing the device lifetime [2]; (2) need to encapsulate the
34 phosphors in a resin to obtain a mechanically stable layer, the binder leading to accelerated ageing of
35 the wLEDs [3,4]; (3) poor coupling with blue nanostructured chips that are now emerging, such as
36 InGaN nanowire arrays for micro-displays [5]. Moreover, with regard to the latter point in particular,
37 the use of micron-sized phosphors is unsuitable to implement additive manufacturing techniques,

38 which are quickly rising as a potential benefit to wLED developments. Indeed, the performance of
39 modern LED devices can indeed be significantly improved by 2D and 3D printing, particularly by
40 specially designed nano/micro-structures within LEDs requiring, which needs nanophosphors. Thus,
41 to overcome these drawbacks, the use of nanophosphors with particle sizes smaller than 100 nm is
42 required: (1) to control light scattering and enhance the light extraction that is directly associated with
43 the emission efficiency of wLEDs devices; (2) to perform the phosphor shaping without any binder,
44 e.g. by preparing pure nanoceramics of pure phosphors as also targeted by researchers working on
45 glass-ceramic phosphors [6], and to obtain a better coupling with nanostructured semi-conducting
46 heterostructures [7]; (3) to deposit phosphor layers by 2D and 3D printing on nanostructured diodes by
47 ink-jet techniques, involving phosphor nanocrystals (NCs with diameter < 100 nm) dispersed in
48 solution with very good colloidal stability [8]. Another problem with the YAG:Ce phosphors, that is
49 unrelated to particle size, is their yellow emission, leading to wLEDs exhibiting poor color rendering
50 indexes (CRI), characterized by a cold white emission, uncomfortable for human eyes.
51 In this article, we review different chemical methods for the preparation of YAG:Ce NCs, pointing out
52 their size and crystal quality, their aggregation or agglomeration state [9] and finally their internal
53 luminescence quantum yield (iQY). We then focus on other garnet-type nanophosphors whose
54 spectroscopic properties are more appropriate to elaborate warm white LED lighting.

55

56 2 Synthesis of YAG:Ce nanocrystals

57 Solid-state reaction, used to synthesize commercial YAG:Ce powder, requires high temperature
58 treatment (> 1500°C), which is energy-consuming and leads to micron-sized phosphors with an iQY
59 of 87 % [10,11,12]. To synthesize YAG:Ce NCs, several approaches can be envisioned: (1) a top-down
60 strategy, consisting in intensive grinding of micron-sized powder, but it induces a large number of
61 surface defects acting as luminescence quencher; (2) bottom-up approaches, including Chemical Vapor
62 Deposition [13], Pulsed Laser Deposition [14] or wet chemical routes, such as combustion [15,16,17],
63 co-precipitation [18,19,20], sol-gel [21,22], modified Pécchini [23] and solvothermal [24,25,26] routes.
64 In the following, we will detail the main wet chemical routes, which present the advantage of being
65 cheaper than the others. Moreover, these wet chemical processes allow to achieve balanced mixture of
66 precursors at the molecular level, resulting in the lowering of the nanoYAG crystallization temperature.

67 2.1 Combustion syntheses

68 This YAG:Ce NC synthesis route consists in an exothermic reaction between a fuel, typically urea or
69 glycine as reducing agent, and yttrium, aluminum and cerium nitrates as oxidizers [27,28,29]. The
70 combustion is initiated by an external heating (~500°C) followed by a high temperature treatment
71 around 1000°C to yield pure YAG and improve the Ce³⁺ incorporation into the matrix [16,30,31]. The
72 combustion step leads to large and irregular particles containing lots of pores because of the gases
73 liberated during the fuel combustion, while the high-temperature treatment required to crystallize the
74 YAG phase results in strong particle sintering, which leads to highly agglomerated NCs [16,32]. An
75 alternative consists in mixing yttrium nitrate with glycine and aluminum nitrate with urea to avoid a
76 subsequent heat treatment and reduce the NC agglomeration [29,31,33]. It led to 40 nm particles
77 agglomerated in 100 to 200 nm clusters, presenting an iQY of 54 % [34]. The main issue of the
78 combustion technique is the temperature inhomogeneity through the reacting mixture with the
79 occurrence of the so-called “hot spots”. This leads to inhomogeneities in chemical composition with
80 the formation of spurious phases such as YAlO₃ and Y₄Al₂O₉ [15, 30], but also inhomogeneities in
81 particle morphology with a broad size distribution. This is due to heterogeneous nucleation, growth

82 and coalescence mechanisms, which are enhanced by the further high temperature treatment. In 2017,
83 Abd *et al.* managed to synthesize YAG:Ce NCs through a shortened combustion synthesis, thanks to
84 laser-assisted or microwave-assisted reaction [32,35]. This latter yielded well-crystallized YAG:Ce
85 NCs of about 60 nm in one-step with reduced, but still present, NC agglomeration (**Figure 1.a**) [36].
86 To conclude, the combustion synthesis is a rapid and simple process requiring high temperature
87 treatment to obtain crystalline NCs with high luminescence intensity, but with a severe agglomeration.

88 2.2 Co-precipitation methods

89 Chemical precipitation syntheses of YAG:Ce NCs have been commonly used by the normal strike
90 technique or by the reverse strike route through the pH control of aqueous solutions. For normal strike,
91 a basic solution (ammonium bicarbonate, ammonium hydroxide, etc, as precipitants) is added into an
92 acidic one (nitrate precursor solution) or the other way around (reverse strike) [37,38,39]. Other routes
93 used alcohol-water as precipitant solvent, the alcohol acting also as surfactant reducing initial NC
94 aggregation [40]. The obtained precipitate (hydroxides, carbonates, hydroxycarbonates...) requires a
95 subsequent calcination at a temperature superior to 1000°C to obtain pure nanoYAG with moderate to
96 severe agglomeration and wide size dispersion: from a few hundreds of nanometers to micrometer NC
97 agglomerates [41,42,43]. To tackle these issues, Qiu *et al.* showed that acidic conditions led to smaller
98 YAG:Ce crystal size since it fosters the precipitation of Al³⁺ (aggregation of 65 nm crystals) and narrow
99 size dispersion, alongside with higher emission intensity [41]. To reduce even more the agglomeration
100 of YAG:Ce NCs, surfactants, such as steric stabilizers (polyethylene glycol, PEG10000), electric
101 stabilizers ((NH₄)₂SO₄, C₁₂H₂₅SO₄Na), or other dispersing agents (e.g. graphene oxide nanosheets)
102 [44,45,46,47,48] were involved in the initial solutions, resulting after ~1000°C calcination in
103 nanoYAG (about 70 nm) with narrow particle size distribution, spherical shapes, moderate NC
104 agglomeration and enhanced PL emission intensity. With no surfactant but by combining
105 ultrasonication during the addition of the initial solution to the precipitant and microwave heating, Si
106 *et al.* managed to produce uniformly dispersed 18 nm (900°C) to 43 nm (1100°C, **Figure 1.b**) YAG
107 particles depending on the annealing temperature, with reduced agglomeration [49]. Very recently,
108 Gaiser *et al.* published an original two-step approach, including first the formation of particles in ionic
109 liquid solution, followed by a heat-treatment at 600°C to crystallize YAG:Ce NCs embedded in a LiCl
110 matrix, preventing their agglomeration. This process results in individual NCs with an average size
111 below 100 nm, presenting a iQY of 51 % [50].

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

115 2.3 Sol-gel route and modified Pécini method

116 The sol-gel synthesis of YAG:Ce NCs involves metal alkoxides as Y, Al precursors (which can be
117 partly replaced by metal salts, generally Y or Ce nitrates) in alcoholic or aqueous solutions, that are
118 converted into a gel through hydrolysis and condensation reactions (~ 60°C) [21,51,52,53]. The
119 resulting gels are then dried into powders and further annealed at around 1000°C, leading to YAG NCs
120 with different agglomeration levels depending on temperature, duration and atmosphere used during
121 heating treatments [22,54,55]. Several conditions have been implemented to have a better control over
122 the YAG:Ce particle size. In 2018, Singlard *et al.* managed to control the YAG:Ce NC size from 55 to
123 123 nm with metal concentration variation [56]. There are only few papers reporting iQY values for
124 the sol-gel prepared YAG:Ce NCs. Murai *et al.* reported a thin YAG:Ce film formed of coalesced
125 particles with a iQY of 65 % via an epoxide-catalyzed sol-gel method with a 1600°C heating treatment
126 [57].

127 An important drawback of the sol-gel route is due to the high reactivity of the alkoxides precursors,
128 with the risk of significant metal inhomogeneity in the gel. Thus, the modified P echini method was
129 used as an alternative to overcome the sol-gel route limitations, particularly to improve the control of
130 YAG:Ce NC size. In the modified P echini method, the metal ions are first chelated in aqueous
131 solutions, usually by citric acid, which reacts then with a polyalcohol (typically ethylene glycol) giving
132 viscous resins, through poly-esterification reactions, where metal ions are highly dispersed. After an
133 annealing step, it leads to a lowered size of 50 to 70 nm NCs with agglomerates up to a few hundreds
134 of nanometers (**Figure 1.c** for a sample annealed at 1030 C) [58,59,60,61]. Mamonova *et al.* in 2016
135 synthesized freely dispersed individuals NCs of about 100 nm with increased emission intensity
136 through an additional annealing in molten salts [62].

137 Although the sol-gel route involves low cost products and is broadly developed to synthesize rare-earth
138 doped metal oxides [63], it is a complex method requiring control over a large number of parameters:
139 pH, temperature, annealing parameters, reactant concentration, additives, complexing agent. It leads to
140 poor control on the YAG:Ce NC size and do not allow to get YAG NC dispersion in a solvent, an
141 essential step for further nanophosphor shaping. The modified P echini method, a simpler alternative to
142 sol-gel route allowing a deeper control over the NCs size, nevertheless requires high temperature
143 treatments, favoring NC coalescence and agglomeration, which are not usually sufficient to remove all
144 the organic residues [23].

145 **2.4 Solvothermal method**

146 The conventional solvothermal route consists to heat in an autoclave (up to 300 C) a precursor solution
147 composed of yttrium and cerium acetates, aluminum isopropoxide and 1.4-butanediol used as solvent.
148 An autogenous pressure builds inside the autoclave up to about 60 bars in a few hours [64,65,66]. The
149 combination of pressure and temperature leads to non-equilibrium conditions, allowing the
150 nanocrystallization of YAG:Ce NCs, without any subsequent thermal treatment of nanopowders. This
151 represents an important advantage to avoid NC coalescence and agglomeration that inevitably occur
152 during the final high temperature treatments required for the previous synthesis routes. Depending on
153 the reaction time and temperature, the conventional solvothermal method commonly yields YAG:Ce
154 particles from 20 to 100 nm [25,67,68,69]. These particles are usually composed of spherical NCs of
155 a few nanometers with the formation of large cauliflower-shape agglomerates (**Figure 1.d**) [68]
156 exhibiting PL iQY between 20 and 30% [25,68,70].

157 To improve the crystal quality and, subsequently the iQY of YAG:Ce NCs, Revaux *et al.* proposed a
158 protected annealing method consisting in annealing at 1000 C YAG:Ce NCs previously dispersed in a
159 porous silica, which preserves their nanometer size of YAG:Ce [71]. This method led to 60 nm highly
160 crystalline and well-dispersed NCs with an iQY of 60%. However, to retrieve the NCs, silica should
161 be dissolved by hydrofluoric acid, highly toxic, which is not appropriate for any industrial
162 development. In 2017, Odziomek *et al.* managed to synthesize ultra-small individual and
163 monodispersed YAG:Ce NCs (4-5 nm) (**Figure 1.e**) by dehydrating the starting precursors and adding
164 diethylene glycol [72]. The addition of a co-solvent contributes to size reduction and minimized NC
165 aggregation. Recently, Dantelle *et al.* introduced a modified solvothermal process by combining high
166 temperature (400 C) and steady high pressure (200 bar) to produce well-crystallized individuals
167 YAG:Ce NCs with iQY of 40 % (**Figure 1.f**) [26].

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

172

173 3 New nanophosphors for white LED lighting

174 Although YAG:Ce nanophosphors have been at the center of attention for the development of
 175 nanostructured LED lighting, other garnet-type nanophosphors are developed, using the synthesis
 176 methods presented above. Indeed, the combination of YAG:Ce and InGaN blue diode leads to a so-
 177 called “cold white” LED lighting, which can be responsible for eye discomfort and even, at high power,
 178 for retina damage [73]. A great amount of work has been made to propose phosphors, at the micron
 179 scale, that would present a red-shifted emission, leading to a warmer white light [74,75]. Due to its
 180 stable chemical and optical properties, garnet-type structure provides excellent hosts, able to
 181 incorporate various lanthanide and transition metal ions [76,77,78]. Two strategies have been followed:
 182 (1) The first one consists in synthesizing new Ce^{3+} -doped garnet compounds whose emission is shifted
 183 due to the crystal field effect of the host matrix. Indeed, Ce^{3+} emission is based on the radiative de-
 184 excitation from 5d levels, sensitive to the local environment, to 4f levels, and thus varies with the host
 185 nature; (2) The second strategy consists in modifying the nature of the doping ions and incorporating
 186 other lanthanide or transition metal ions whose electronic transitions fall in the red range.
 187 With the need for miniaturization and better coupling with nanostructured diodes, the search for new
 188 nanophosphors with a redder emission has been launched [79], with the challenge to control the phase
 189 purity of these new compounds, as well as their NC size and crystal quality to obtain high PL efficiency.

190 3.1 New garnet-type nanophosphors doped with Ce^{3+}

191 According to Wu *et al.* [80], and more recently to Ueda and Tanabe [81], the emission wavelength of
 192 Ce^{3+} is directly related to the distortion of the dodecahedral site occupied by Ce^{3+} , in the different
 193 garnet structures. Through thorough studies at the micron scale, it was shown that the bigger the site
 194 distortion, the more red-shifted the emission. Based on the numerous studies at the micron-sized level,
 195 several garnet-type nanophosphors have been developed. As shown on **Figure 2**, for nanophosphors,
 196 the substitution of Y^{3+} by Gd^{3+} ($r_{\text{Y}^{3+}} = 1.019 \text{ \AA}$ vs. $r_{\text{Gd}^{3+}} = 1.053 \text{ \AA}$, coordination number, CN = 8)
 197 induces a red-shift of the emission of about 10 nm [82,83], whereas the Y^{3+} substitution by Lu^{3+}
 198 ($r_{\text{Lu}^{3+}} = 0.977 \text{ \AA}$) shifts the emission towards the blue region [84,85]. Meanwhile, the substitution of
 199 octahedral aluminum ($r_{\text{Al}^{3+}} = 0.535 \text{ \AA}$, CN = 6) by Ga^{3+} ($r_{\text{Ga}^{3+}} = 0.66 \text{ \AA}$, CN = 6) induces a 10 nm blue-
 200 shift of the emission [82] and, in $\text{Gd}_3\text{Sc}_2\text{Al}_3\text{O}_{12}:\text{Ce}^{3+}$ NCs doped with 10 mol.% Ce^{3+} , a significant red-
 201 shift of about 50 nm is observed [86]. These nanoscale evolutions follow the trends obtained at the
 202 micron scale and can be explained by the influence of the host crystal field, leading to different
 203 splittings of the 5d levels of Ce^{3+} responsible for the emission. Other garnets, such as Ce^{3+} -doped
 204 silicate garnet $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ [87], can be good alternatives to provide red emission. Note that, at present
 205 time, most of the garnet-type nanophosphor work reported in the literature deal with strongly
 206 agglomerate particles synthesized mainly by the sol-gel method, which is not entirely satisfactory for
 207 the use of NCs in nanostructured white LED lighting.

208 Interestingly, as the synthesis methods employed to elaborate NCs involve non-equilibrium conditions,
 209 YAG:Ce NCs can be doped with higher concentration than their bulk equivalent. Thus, up to 13 mol.%
 210 Ce was introduced in YAG NCs produced by low-energy cluster beam deposition [88], and up to 30
 211 mol.% using auto-combustion method [89]. Although the maximal quantum efficiency is usually
 212 obtained for a low doping concentration, high doping could allow to redshift the emission. Indeed, in
 213 Ce^{3+} -doped YAG and $\text{Gd}_3\text{Sc}_2\text{Al}_3\text{O}_{12}$, emission is redshifted by increasing the cerium concentration
 214 from 1 mol. To 10 mol.% [88,90]. This phenomenon can be an advantage for tuning the emission
 215 wavelength while using garnet-type nanophosphors and is explained by the fact that Ce^{3+} ions ($r_{\text{Ce}^{3+}} =$
 216 1.143 \AA) substitutes Y^{3+} , inducing more distortion within the crystal lattice.

217 3.2 Garnet-type nanophosphors doped with other Ln³⁺ ions

218 The second strategy to obtain phosphors with a redshifted emission consists in introducing other doping
219 ions than Ce³⁺: other trivalent lanthanide ions, divalent lanthanide ions or transition metal ions. A large
220 number of papers, dealing with garnets at the micron scale, report such doping modifications
221 [76,77,91]. At the nanoscale, the literature is scarcer and mainly reports nanophosphors doped with
222 trivalent lanthanide ions (Gd³⁺, Eu³⁺, Sm³⁺, Dy³⁺, Tb³⁺), exhibiting electronic intra-configurational
223 transitions in the red range. Such ions are incorporated as dopant or co-dopant in the garnet-type
224 nanophosphors and provide red emission components [92,93,94,95,96,97] (**Figure 2**).

225 The utility of these nanophosphors for wLED lighting can be evaluated by the calculation of their color
226 coordinates (x,y), the correlated color temperature (CCT) and the color rendering index (CRI). The
227 standard illuminant, corresponding to the average daylight, presents color coordinates of (0.31,0.33)
228 and a CCT around 6500 K [98]. YAG:Ce-based wLEDs, give CCT values higher than 7000 K (“cold
229 white”) and a maximal CRI of ~ 80, according to Ce³⁺ concentration and phosphor thickness [99].
230 Thanks to their red emission component, the above-mentioned compounds can be combined to semi-
231 conducting diodes and provide better CCT and CRI. For instance, an optimized wLED combining
232 YAG:Ce and YAG:Ce,Gd nanophosphors with a InGaN chip exhibits color coordinates of (0.31,0.32),
233 a CCT of 6564 K and a CRI of 86 [94]. Another example is Dy³⁺-doped Lu₃Al₅O₁₂ nanophosphors,
234 showing interesting color coordinates (0.317, 0.321) and a CCT of 6322 K, close to the ideal white
235 light [97].

236 In comparison to micron-sized phosphors, additional challenges appear when working with
237 nanophosphors due to the crystal size and the synthesis methods involved. Indeed, if the Ln³⁺ emission
238 wavelength is not affected by the size reduction, the PL efficiency and energy transfer between doping
239 ions can be different due to surface traps and volume defects [26,100]. Moreover, the control of the
240 oxidation state at the nanoscale is problematic. Indeed, when working with micron-sized powder,
241 typical annealing under controlled atmosphere can be performed to stabilize the oxidation state of the
242 doping ion, as for Ce³⁺-doped YAG [10] and also in Eu²⁺-doped YAG [101]. To obtain NCs, post
243 annealing should be avoided, making the control of the oxidation state more complex. For instance,
244 when using solvothermal method, Dantelle *et al.* showed by X-ray absorption spectroscopy that a non-
245 negligible fraction of cerium ions (nearly 50 %, depending on the synthesis temperature) were oxidized
246 [26]. To preserve the right oxidation state while elaborating NCs, more complex strategies should be
247 proposed. A recent study proposes the bubbling of a reducing gas in a solution prior to solvothermal
248 treatment, preventing partially the oxidation of Ce³⁺ during the heat treatment [102].

249

250 4 Conclusion

251 Several solution-based methods (co-precipitation, sol-gel, solvothermal, etc) have been developed for
252 the synthesis of YAG:Ce NCs. However, most of them involve an annealing step at high temperature
253 (typically above 800°C), which induces NC agglomeration and thus prevents their dispersion in
254 solution and their further deposition onto blue LEDs. The solvothermal method, occurring completely
255 in solution and requiring no further annealing, appears as an efficient way to produce non-agglomerated
256 NCs. However, many parameters (pressure, temperature, solvent, etc) should be controlled to control
257 YAG:Ce nanocrystallization and to produce highly luminescent NCs. Aside the YAG:Ce
258 nanophosphor, other garnet-type nanophosphors are developed with the goal of obtaining a red-shift
259 emission. This emission shift can be obtained by considering either another garnet-type matrix or other
260 doping ions, on the model of works performing at the micron scale. However, each new compound

261 requires thorough nanocrystallization study to control the size, morphology and PL properties. Hence,
262 the synthesis of nanophosphors for white LED lighting still remains a real challenge. Perspectives also
263 include nanophosphor shaping, using low cost techniques based on solution such as inkjet printing onto
264 semi-conducting chips. The development of such wLED devices should allow better control of light
265 scattering, minimization of optical losses, better coupling with nanostructured blue diodes for enhanced
266 efficiency and miniaturization of the devices.

267

268 **5 Conflict of Interest**

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

271

272 **6 Author Contributions**

273 All authors have contributed equally to writing this mini-review.

274

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277 their research on nanophosphors.

278

279 **8 Figure captions**

280 **Figure 1.** Microscopy images of YAG:Ce NCs prepared (a) by combustion, reproduced from *Opt. Eng.*
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282 *Nanomater.* (2014) 2014, 408910, under the Creative Commons CC BY license; (c) by modified
283 Péchini method, reproduced from *Sci. Rep.* (2016) 6, 22238, under the Creative Commons CC BY
284 license; (d) by conventional solvothermal synthesis. Image reproduced from *J. Phys. Chem. B.* (2005)
285 109, 22126, with permission from American Chemical Society, Copyright (2020); (e) by solvothermal
286 synthesis after precursor dehydration and adding diethylene glycol. Image reproduced from *J. Mater.*
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288 solvothermal synthesis, high pressure and steady high temperature. image reproduced from *RSC Adv.*
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290

291 **Figure 2.** Emission range of different garnet-type nanophosphors reported in the literature. The
292 emission range has been defined by considering all emission whose intensity is larger than $I_{max}/2$,
293 with I_{max} the maximal PL emission intensity. The dark blue indicates a strong emission intensity, in
294 comparison to the light blue. No emission intensity comparison can be done among the different
295 nanophosphors.

296

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