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(54) Title: METHOD FOR TREATING A LUMINESCENT MATERIAL COMPRISING ORGANIC LIGANDS

(57) Abstract: The invention relates to a method for treating a luminescent material comprising organic ligands, said method comprising contacting said luminescent material comprising organic ligands with an oxidizing agent. Preferably, the luminescent material is in the form of nanoparticles.



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METHOD FOR TREATING A LUMINESCENT MATERIAL COMPRISING ORGANIC LIGANDS

FIELD OF THE INVENTION

5 [0001] The invention relates to a method for treating a luminescent material comprising organic ligands and to methods for preparing a luminescent composition methods. The invention also relates to a luminescent material and a luminescent composition obtainable by the methods according to the invention, and uses thereof.

BACKGROUND OF THE INVENTION

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[0002] Luminescent materials, for instance if in the form of nanoparticles, may comprise organic ligands. Nanoparticles are most often synthesized in solution, wherein the growth and final size can be controlled. To prevent clustering during or after synthesis and to have additional means to control the growth, it is very common to bind 'organic ligands' or 'capping molecules' to the surface of the nanoparticles. These are organic molecules, that either by their electrostatic charge or just by their 'bulkiness', or by a combination of these, prevent clustering of the particles.

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[0003] For certain applications it is desirable to remove the organic ligands from the luminescent material. This is for instance the case, if it is aimed to allow non-radiative energy transfer (sometimes also referred to as Fluorescent Resonance Energy Transfer, FRET) from a sensitizer material to a light emitting material, in which case these materials should be in close enough proximity.

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[0004] Although various methods are known in literature to remove or replace organic ligands, it is not a straight-forward process to do so and it can be very dependent on the exact conditions, kind of nanoparticles and organic ligands which method works. Especially in the case of nanoparticle mixtures, with different kinds of particles and/or organic ligands such a selective method is often not desirable. An example of such a selective method is described in *Nano Lett.*, 2011, 11 (12), pp 5356–5361.

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[0005] A less-selective known method is to use acids, like HCl (typically around 0.1M) to remove the organic ligands. The use of HCl to remove organic ligands is described in *Wang et al, Tuning upconversion through Energy Migration in Core-Shell Nanoparticles, Supplementary Information, Nature Materials (2011) 1-35*. However, strong acids can damage or even dissolve the nanoparticle surface, which results in reduced luminescence efficiencies.

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[0006] In view of the above it is an object of the invention to provide method for removing organic ligands from a luminescent material, preferably in the form of nanoparticles, which does not or minimizes damage to the particles and which is less selective, i.e. can be applied to a wide variety of luminescent materials and organic ligands.

5 [0007] In unpublished PCT application no. PCT/EP2018/056660, the present inventors have described, amongst others, compositions comprising a light emitting material and a sensitizer material, wherein the light emitting material and the sensitizer material are selected such that the sensitizer material has an emission spectrum which overlaps at least partly with one or more excitation bands of the light emitting material and wherein the light emitting material and sensitizer
10 material are so arranged to each other to allow non-radiative energy transfer from the sensitizer material to the light emitting material. This application also describes methods for the preparation thereof.

[0008] The skilled person will understand that non-radiative energy transfer (sometimes also referred to as Fluorescent Resonance Energy Transfer, FRET) from the sensitizer material to
15 the light emitting material involves the non-radiative transfer of energy from an excited sensitizer ion in the sensitizer material to an acceptor (or emitter) ion in the light emitting material. It is evidenced by increased selective excitation of the sensitizer ion in the sensitizer material, resulting in increased emission from an emitter ion in the light emitting material.

[0009] The present application discloses further improved luminescent compositions and
20 luminescent materials and further improved methods from the preparation thereof.

SUMMARY OF THE INVENTION

[0010] In a first aspect, the invention provides a method for treating a luminescent material
25 comprising organic ligands, said method comprising contacting said luminescent material with an oxidizing agent.

[0011] Contacting the luminescent material comprising organic ligands with the oxidation agent is found to result in oxidation of at least part of the organic ligands. Oxidation of the organic ligands has been found to result in their effective removal from the luminescent material. Without
30 wishing to be bound by any scientific theory it is believed that the oxidation breaks down the organic ligands enabling the residues to dissolve.

[0012] If the luminescent material is in the form of nanoparticles, the efficient removal of organic ligands enables to obtain particles which are in close proximity with one another. This is particularly advantageous if it is desired obtain a material which allows non-radiative energy transfer (FRET) from a sensitizer material to a light emitting material.

5 [0013] In a second aspect, the invention provides a method for treating a luminescent material comprising organic ligands, said method comprising:

- (a) removing at least part of said organic ligands from the luminescent material; and
- (b) after (a), annealing said luminescent material

10 [0014] In a third aspect, the invention provides a method for preparing a luminescent composition, said method comprising:

- (i) providing a first luminescent material and a second luminescent material;
- (ii) dispersing said first luminescent material and said second luminescent material in a liquid;
- (iii) optionally, removing organic ligands from said first luminescent material and/or from said second luminescent material;
- 15 (iv) removing said liquid, resulting in a dried product, wherein said removing comprises evaporation; and
- (v) annealing said dried product.

[0015] In a fourth aspect, the invention provides a method for preparing a luminescent composition, said method comprising:

- 20 - providing a composition comprising a first luminescent material and a second luminescent material, wherein said first luminescent material and said second luminescent material are selected such that said second luminescent material has an emission spectrum which overlaps at least partly with one or more of excitation bands of said first luminescent material; and wherein said first luminescent material and said second luminescent material
- 25 are so arranged to each other to allow non-radiative energy transfer from said second luminescent material to said first luminescent material; and
- annealing said composition.

[0016] There is further provided a luminescent material or composition obtainable by the methods according to any of the aspects of the invention, devices and systems comprising these, and uses thereof.

5 BRIEF DESCRIPTION OF THE DRAWINGS

[0017] FIGURE 1 provides FTIR spectra of LaPO_4 nanoparticles before and after organic ligand removal. Peaks around 1450 and 2950 cm^{-1} indicate C-H bending and stretching from the organic ligands respectively.

10 [0018] FIGURE 2 provides emission spectra from $\text{LaPO}_4:\text{Eu}^{3+}/\text{LaPO}_4:\text{Tb}^{3+}$ mixtures, mixed in a 1 : 1 weight ratio. Excitation at 484.5 nm .

[0019] FIGURE 3 provides emission spectra from $\text{LaPO}_4:\text{Eu}^{3+}/\text{LaPO}_4:\text{Tb}^{3+}$ mixtures, mixed in a 1 : 1 weight ratio. Excitation at 395 nm .

[0020] FIGURE 4 provides excitation spectra from $\text{LaPO}_4:\text{Eu}^{3+}/\text{LaPO}_4:\text{Tb}^{3+}$ mixtures, mixed in a 1 : 1 weight ratio. Emission at 695 nm .

15 [0021] FIGURE 5 shows Tb^{3+} decay in $\text{LaPO}_4:\text{Eu}^{3+}/\text{LaPO}_4:\text{Tb}^{3+}$ mixtures, mixed in a 1:1 weight ratio. Excitation at 355 nm , emission at 542 nm .

[0022] FIGURE 6 provides Eu^{3+} emission spectra from $\text{LaPO}_4:\text{Eu}^{3+}$ (5%)/ $\text{LaPO}_4:\text{Tb}^{3+}$ (40%) mixtures, mixed in a 1:1 weight ratio, before and after annealing at $600\text{ }^\circ\text{C}$. Excitation in the Tb^{3+} , at 484.5 nm .

20 [0023] FIGURE 7 provides Eu^{3+} excitation spectra of $\text{LaPO}_4:\text{Eu}^{3+}$ (5%)/ $\text{LaPO}_4:\text{Tb}^{3+}$ (40%) mixtures, mixed in a 1:1 weight ratio, before and after annealing at $600\text{ }^\circ\text{C}$. Emission measured at 697 nm . Spectra are normalized to the 395 nm direct Eu^{3+} excitation line.

[0024] FIGURE 8 shows a visualization of annealing YAG:Ce nanoparticles.

25 [0025] FIGURE 9 shows a very schematic cross-section of YAG:Ce nanoparticles in the presence of YAG:Eu nanoparticles, before and after annealing.

[0026] FIGURE 10 shows a very schematic cross-section of YAG:Ce nanoparticles, before shell growth, after shell growth, and after annealing.

[0027] FIGURE 11 shows a very schematical cross-sectional view of YAG:Ce and YAG:Eu nanoparticles which have been subjected to shell growth.

[0028] FIGURE 12 shows a very schematic cross-sectional view of YAG:Ce and YAG:Eu nanoparticles which have been subjected to shell growth, before and after annealing.

[0029] FIGURE 13 shows a first embodiment of a composition which may be used in the method according to an aspect of the invention.

5 [0030] FIGURE 14 shows a second embodiment of a composition which may be used in the method according to an aspect of the invention.

[0031] FIGURE 15 shows a very schematical cross-sectional view through a nanoparticle which may be used in the method according to an aspect of the invention.

10 [0032] FIGURE 16 shows a very schematical cross-sectional view through a nanoparticle which may be used in the method according to an aspect of the invention.

[0033] FIGURE 17 shows a very schematical cross-sectional view through a nanoparticle which may be used in the method according to an aspect of the invention.

[0034] FIGURE 18 shows a very schematical cross-sectional view through a nanoparticle which may be used in the method according to an aspect of the invention.

15 [0035] FIGURE 19 shows the overlap of the emission spectrum of $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ (0.65%) (LuAG) (upper trace) as second luminescent material and of excitation bands of $\text{LaPO}_4:\text{Tb}$ (lower trace) as first luminescent material.

[0036] FIGURE 20 shows the overlap of the emission spectrum of $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ (0.65%) (LuAG) (upper trace) as second luminescent material and of excitation bands of $\text{Li}_3\text{Ba}_2(\text{La}_{0.6}\text{Eu}_{0.4})_3(\text{MoO}_4)_8$ (lower trace) as first luminescent material.

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DETAILED DESCRIPTION OF THE INVENTION

First aspect of the invention

25 [0037] The first aspect of the invention provides a method treating a luminescent material comprising organic ligands, said method comprising contacting said luminescent material comprising organic ligands with an oxidizing agent.

Luminescent material comprising organic ligands

[0038] The luminescent material comprising organic ligands is not limited to a particular luminescent material having organic ligands attached to its surface. As is known to the skilled person, ligands can also be referred to as capping molecules (or a capping agent).

5 [0039] As is known to the skilled person, organic ligands are generally used to control growth and to avoid clustering of particles, in particular of nanoparticles. The organic ligands may be any organic ligands suitable for this purpose. Examples of organic ligands include fatty acids (including salts and esters thereof), amines, polyols, for instance oleic acid, oleyl amine, oleate, tributylamine and (poly) ethylene glycol.

10 [0040] Preferably, the luminescent material is provided in the form of nanoparticles. Any suitable nanoparticles may be used. Suitable nanoparticles include particles of which at least one dimension is at a nanometer scale, preferably ≤ 100 nm. More preferably, the D50 of the nanoparticle diameter is ≥ 1 nm and ≤ 50 nm, most preferably ≥ 2 nm and ≤ 10 nm. The D50 may suitably be determined using transmission electron microscopy (TEM).

15 [0041] The luminescent material may comprise a host lattice which may be doped with ions.

[0042] Any suitable host lattice may be used. The host lattice may for instance be selected from the group consisting of oxides, fluorides, nitrides, borates, garnets, molybdates, phosphates, vanadates, chlorides, sulfides, selenides, silicates, aluminates, oxyfluorides, fluorosilicates, oxychlorides, oxynitrides, oxysulfides, oxyselenides, fluorochlorides, and fluorobromides or combinations of these or another inorganic host material in which optically active lanthanide ions can be incorporated.

20 [0043] In a preferred embodiment, the host lattice is an oxide, garnet, phosphate, vanadate or combination of these such as Y_2O_3 , YVPO_4 , YVO_4 or LaPO_4 or $\text{Y}_3\text{Al}_5\text{O}_{12}$ ("YAG") or $\text{Lu}_3\text{Al}_5\text{O}_{12}$ ("LuAG").

25 [0044] Any suitable optically active (e.g. luminescent) ion may be used. The host lattice may for instance be doped with one or more ions selected from the group consisting of Eu^{3+} , Tb^{3+} , Mn^{4+} , Eu^{2+} , Pb^{2+} , Bi^{3+} and Ce^{3+} , preferably Ce^{3+} or Eu^{3+} , Mn^{4+} and Tb^{3+} , most preferably Eu^{3+} or Ce^{3+} .

30 [0045] In a preferred embodiment the luminescent material is a material disclosed herein below as first luminescent material and/or second luminescent material.

Oxidizing agent

[0046] The method according to the first aspect of the invention comprises contacting the luminescent material comprising the organic ligands with an oxidizing agent. Any suitable oxidizing agent may be used. Suitable oxidation agents may include any compound or combination of compounds, preferably in a solution, capable of oxidizing at least part of the organic ligands. Preferably, the oxidation agent is selected such that it is capable of oxidizing carbon present in the carbon chain of the organic ligands. Without wishing to be bound by any scientific theory, it is believed that as a result of the oxidation the organic ligands break down enabling the residues to dissolve and be removed in a simple and efficient manner, preferably using one or more washing steps.

[0047] Preferably the oxidizing agent has a standard reduction potential > 1 Volt.

[0048] The oxidizing agent may for example be selected from the group consisting of an inorganic peroxide (preferably H_2O_2), Fenton's reagent, nitric acid (HNO_3) and nitrate compounds, sulfuric acid (H_2SO_4), peroxydisulfuric acid ($\text{H}_2\text{S}_2\text{O}_8$), peroxymonosulfuric acid (H_2SO_5), chlorite, chlorate, perchlorate, and other analogous halogen compounds, Fluorine (F_2), chlorine (Cl_2), and other halogens, hypochlorite and other hypohalite compounds, hexavalent chromium compounds such as chromic and dichromic acids and chromium trioxide, pyridinium chlorochromate (PCC), and chromate/dichromate compounds, permanganate compounds such as potassium permanganate, sodium perborate, nitrous oxide (N_2O), nitrogen dioxide/dinitrogen tetroxide ($\text{NO}_2 / \text{N}_2\text{O}_4$), potassium nitrate (KNO_3).

[0049] Preferably, the oxidizing agent comprises H_2O_2 . Preferably, the oxidizing agent comprises H_2O_2 in combination with NH_4OH or H_2SO_4 , more preferably H_2O_2 in combination with NH_4OH . Preferably, the oxidation agent is present in a solution, preferably an aqueous solution.

Contacting the luminescent material comprising organic ligands with the oxidizing agent

[0050] The luminescent material comprising organic ligands may be contacted with the oxidizing agent in any suitable manner.

[0051] Preferably, the luminescent material comprising organic ligands is contacted with the oxidizing agent in the presence of a solution comprising the oxidizing agent.

[0052] Any suitable solution in which the luminescent material comprising the organic ligands may be dispersed may be used. Preferably, the solution comprises water or an alcohol (preferably methanol or ethanol) or a mixture thereof.

[0053] Preferably, the solution comprises NH_4OH , more preferably the solution comprises NH_4OH and H_2O_2 . Preferably, the solution comprises NH_4OH and H_2O_2 in a weight ratio between 8 : 1 and 2 : 1 most preferably in a weight ratio of about 3:1.

[0054] Preferably, the solution comprising NH_4OH and H_2O_2 is at a temperature of between 60 and 90 °C, preferably about 70 °C.

[0055] In a preferred embodiment, the luminescent material comprising the organic ligands, preferably luminescent material in the form of nanoparticles, is dispersed in a first solution, for instance in water or an alcohol (e.g. methanol or ethanol) or a mixture thereof. The first solution may then be combined with the oxidizing agent and/or with a solution comprising the oxidizing agent. For instance, the oxidizing agent and/or a solution containing the oxidizing agent may be added to the first solution containing the luminescent material.

[0056] Contacting the luminescent material comprising the organic ligands with the oxidizing agent may be performed at any suitable temperature and during any suitable period. The skilled person is able to determine optimal conditions. In a preferred embodiment, in particular if the oxidizing agent is H_2O_2 which is present in a NH_4OH solution, contacting the luminescent material comprising the organic ligands with the oxidizing agent may for instance be effected for 15-120 minutes.

Recovering the luminescent material (from the solution)

[0057] The method may comprise separating said luminescent material from the oxidizing agent.

[0058] Preferably, the method comprises recovering the luminescent material from the solution. This may be achieved in any suitable manner.

[0059] Preferably, recovering the luminescent material from the solution comprises gravity separation (preferably centrifugation) and/or drying by evaporation.

[0060] Preferably, recovering the luminescent material from the solution comprises washing the luminescent material using a washing liquid and recovering the luminescent material from the washing liquid. Preferably, recovering the luminescent material from the washing liquid comprises gravity separation (preferably by centrifugation) and/or drying by evaporation.

[0061] Preferably, recovering the luminescent material from the solution and/or from the washing liquid comprises at least drying by evaporation. Drying by evaporation may be performed in any suitable manner, for instance in an oven and/or under vacuum.

[0062] Preferably the method according to the first aspect of the invention comprises:

(i) providing a luminescent material comprising organic ligands;

(ii) contacting the luminescent material with an oxidizing agent in the presence of a solution comprising the oxidizing agent; and

(iii) recovering the luminescent material from the solution, wherein said recovering comprises

(a) gravity separation, preferably centrifugation, to separate the luminescent material from at least part of the solution;

(b) washing the separated luminescent material using a washing liquid; and

(c) recovering the luminescent material from the washing liquid by gravity separation, preferably centrifugation; and

(d) drying the luminescent material, preferably in an oven.

Mixtures comprising a first luminescent material and a second luminescent material

[0063] In a preferred embodiment, the luminescent material comprising organic ligands is a mixture comprising at least a first luminescent material and a second luminescent material, wherein the first luminescent material and/or the second luminescent material comprise organic ligands. Preferably, the first luminescent material and the second luminescent material comprise organic ligands.

[0064] Thus, in this preferred embodiment, the mixture comprising at least a first luminescent material and a second luminescent material is contacted with the oxidizing agent. This enables to obtain a luminescent material in which the first luminescent material and second luminescent material are present in close proximity. Such close proximity is particularly advantageous if it is desired to obtain a material which allows energy transfer (FRET) from the second luminescent material (or sensitizer material) to the first luminescent material (light emitting material).

[0065] Preferably, the first luminescent material and/or second luminescent material are provided in the form of nanoparticles. More preferably, the first luminescent material and second luminescent material are provided in the form of nanoparticles.

[0066] Preferably, the first luminescent material and the second luminescent material are selected such that the second luminescent material has an emission spectrum which overlaps at least partly with one or more of excitation bands of the first luminescent material. This is in particular advantageous if it is desired to obtain a material which allows energy transfer (FRET) from the second luminescent material to the first luminescent material. The skilled person will understand that, in this preferred embodiment, the first luminescent material functions as light emitting material and the second luminescent material functions as sensitizer material.

[0067] The skilled person is well able to determine the overlap of the spectra based on spectra known in the art or determine the spectra by routine experimentation. For instance, Figure 19 shows the overlap of the emission spectrum of $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ (0.65%) (LuAG) (upper trace) as sensitizer material and of excitation bands of $\text{LaPO}_4:\text{Tb}$ (lower trace) as emitter material. The area of overlap is indicated between dashed lines. Figure 20 shows the overlap of the emission spectrum of $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ (0.65%) (LuAG) (upper trace) as sensitizer material and of excitation bands of $\text{Li}_3\text{Ba}_2(\text{La}_{0.6}\text{Eu}_{0.4})_3(\text{MoO}_4)_8$ (lower trace) as emitter material. The overlapping area is indicated between dashed lines as well.

[0068] Preferably, the first luminescent material is a red emitting material. As used herein the term red emitting material refers to a material which, upon suitable excitation, has one or more emission bands between 600 nm and 700 nm. According to alternative embodiments, the first luminescent material is a material having, upon suitable excitation, one or more emission bands between 700 and 1400 nm (IR-A), between 580 and 600 nm (amber and/or orange), between 560 and 580 nm (yellow), between 510-560 nm (green), between 480 and 510 nm (cyan), between 440

and 480 nm (blue), between 400-440 nm (violet), between 315-400 nm (UV-A), or between 280-315 nm (UV-B).

[0069] Preferably, the first luminescent material is doped with one or more ions selected from the group consisting of Eu^{3+} , Tb^{3+} , Mn^{4+} . Especially preferred is Eu^{3+} or Tb^{3+} .

5 **[0070]** The first luminescent material and second luminescent material may have any suitable host lattice. The host lattice may for instance be selected from the group consisting of oxides, fluorides, nitrides, borates, garnets, molybdates, phosphates, vanadates, chlorides, sulfides, selenides, silicates, aluminates, oxyfluorides, oxychlorides, oxynitrides, oxysulfides, oxyselenides, fluorochlorides, fluorosilicates and fluorobromides or combinations of these or another inorganic
10 host material in which the optically active lanthanide ions can be incorporated.

[0071] In a preferred embodiment, the host lattice of the first luminescent material is an oxide, phosphate, vanadate or a combination thereof, for instance Y_2O_3 , YVPO_4 , YVO_4 or LaPO_4 . Preferably, said preferred host lattice of the first luminescent material is doped with one or more ions selected from the group consisting of Eu^{3+} and Tb^{3+} .

15 **[0072]** In case of Eu^{3+} doping, the first luminescent material may for example have a host lattice doped at a doping level of 2-30% Eu^{3+} , more preferably 5-15% Eu^{3+} . In a preferred embodiment, the first luminescent material has a host lattice doped at a doping level of 5-80% Eu^{3+} , more preferably 10-50% Eu^{3+} . In case Tb^{3+} doping, the first luminescent material may have a host lattice doped at a doping level of 5-100% Tb^{3+} , more preferably 20-50% Eu^{3+} .

20 **[0073]** In an exemplary embodiment, the first luminescent material is selected from the group consisting of $(\text{Ca}, \text{Sr})\text{Ga}_2\text{O}_6:\text{Eu}^{3+}$ (or Tb^{3+}), $(\text{Ca}, \text{Sr}, \text{Ba})\text{La}_2\text{Bi}_2(\text{SiO}_4)_3\text{O}:\text{Eu}^{3+}$ (or Tb^{3+}), $(\text{Ca}, \text{Sr}, \text{Ba})\text{SnO}_3:\text{Eu}^{3+}$ (or Tb^{3+}), $(\text{Ca}, \text{Y}, \text{Gd})\text{MoO}_4:\text{Eu}^{3+}$ (or Tb^{3+}), $(\text{Y}, \text{Gd})\text{BO}_3$ (pseudo-vaterite): Eu^{3+} (or Tb^{3+}), $(\text{Y}, \text{Tb})\text{SiO}_5:\text{Eu}^{3+}$ (or Tb^{3+}), $\text{A-La}_2\text{O}_3:\text{Eu}^{3+}$ (or Tb^{3+}), $\text{Ba}_2(\text{SiO}_4):\text{O}_2-:\text{Eu}^{3+}$ (or Tb^{3+}), $\text{Ba}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{3+}$ (or Tb^{3+}), $\text{Ba}_2\text{Y}(\text{BO}_3)_2\text{Cl}:\text{Eu}^{3+}$ (or
25 Tb^{3+}), $\text{Ba}_3(\text{PO}_4)_2:\text{Eu}^{3+}$ (or Tb^{3+}), $\text{Ba}_3\text{Ca}_3(\text{PO}_4)_4:\text{Eu}^{3+}$ (or Tb^{3+}), $\text{Ba}_3\text{Gd}(\text{BO}_3)_3:\text{Eu}^{3+}$ (or Tb^{3+}), $\text{Ba}_3\text{Gd}_2(\text{BO}_3)_4:\text{Eu}^{3+}$ (or Tb^{3+}), $\text{Ba}_3\text{La}_2(\text{BO}_3)_4:\text{Eu}^{3+}$ (or Tb^{3+}), $\text{Ba}_3\text{V}_2\text{O}_8:\text{Eu}^{3+}$ (or Tb^{3+}), $\text{Ba}_3\text{Y}_2(\text{BO}_3)_4:\text{Eu}^{3+}$ (or Tb^{3+}), $\text{BaB}_8\text{O}_{13}:\text{Eu}^{3+}$ (or Tb^{3+}), $\text{BaBPO}_5:\text{Eu}^{3+}$ (or Tb^{3+}), $\text{BaFCl}:\text{Eu}^{3+}$ (or Tb^{3+}), $\text{BaGd}_2\text{O}_4:\text{Eu}^{3+}$ (or Tb^{3+}), $\text{BaGd}_4\text{Si}_5\text{O}_{17}:\text{Sm}:\text{Eu}^{3+}$ (or Tb^{3+}), $\text{BaGdB}_9\text{O}_{16}:\text{Eu}^{3+}$ (or Tb^{3+}), $\text{BaLaB}_9\text{O}_{16}:\text{Eu}^{3+}$ (or Tb^{3+}), $\text{BaSO}_4:\text{Eu}^{3+}$ (or Tb^{3+}),
30 $\text{BaY}_2\text{F}_8:\text{Yb}:\text{Eu}^{3+}$ (or Tb^{3+}), $\text{BaY}_2\text{Si}_3\text{O}_{10}:\text{Eu}^{3+}$ (or Tb^{3+}), $\text{BaYB}_9\text{O}_{16}:\text{Eu}^{3+}$ (or Tb^{3+}), $\text{BaZr}(\text{BO}_3)_2:\text{Eu}^{3+}$ (or Tb^{3+}), $\text{BaZrO}_3:\text{Eu}^{3+}$ (or Tb^{3+}), b-

BaB₂O₄:Eu³⁺ (or Tb³⁺), B-Gd₂O₃:Eu³⁺ (or Tb³⁺), Ca₂Al(AlSiO₇):Eu³⁺ (or Tb³⁺),
 Ca₂Gd₂(GeO₄)₂O:Eu³⁺ (or Tb³⁺), Ca₂Gd₈(SiO₄)₆O₂:Eu³⁺ (or Tb³⁺), Ca₂Gd₈Si₆O₂₆:Eu³⁺
 (or Tb³⁺), Ca₂La₈(SiO₄)₆O₂:Eu³⁺ (or Tb³⁺), Ca₃(BO₃)₂:Eu³⁺ (or Tb³⁺), Ca₃Al₂O₆:Eu³⁺ (or
 Tb³⁺), Ca₃Gd₂(BO₃)₄:Eu³⁺ (or Tb³⁺), Ca₃La₂(BO₃)₄:Eu³⁺ (or Tb³⁺), Ca₃Y₂(BO₃)₄:Eu³⁺
 5 (or Tb³⁺), Ca₄GdO(BO₃)₃:Eu³⁺ (or Tb³⁺), Ca₅(PO₁₁)₃F:Eu³⁺ (or Tb³⁺), Ca₅(PO₄)₃Br:Eu³⁺
 (or Tb³⁺), Ca₅(PO₄)₃F:(4f-site):Eu³⁺ (or Tb³⁺), Ca₅(PO₄)₃F:(6h-site):Eu³⁺ (or Tb³⁺),
 Ca₅(PO₄)₃OH:Eu³⁺ (or Tb³⁺), CaBPO₅:Eu³⁺ (or Tb³⁺), CaF₂:Eu³⁺ (or Tb³⁺),
 CaLaB₇O₁₃:Eu³⁺ (or Tb³⁺), calcite-CaCO₃:Eu³⁺ (or Tb³⁺), CaO:Eu³⁺ (or Tb³⁺),
 CaSO₄:Eu³⁺ (or Tb³⁺), CaYO(BO₃):Eu³⁺ (or Tb³⁺), C-Gd₂O₃:Eu³⁺ (or Tb³⁺), C-
 10 Lu₂O₃:(C₂):Eu³⁺ (or Tb³⁺), C-Lu₂O₃:(C_{3i}):Eu³⁺ (or Tb³⁺), Cs₂NaYF₆:Tm:Eu³⁺ (or Tb³⁺),
 C-Sc₂O₃:Yb:Eu³⁺ (or Tb³⁺), C-Y₂O₃:Eu³⁺ (or Tb³⁺), Eu³⁺ (or Tb³⁺)[(ttfa)₃(phen)]₀:Eu³⁺
 (or Tb³⁺), Gd_{17.33}(BO₃)₄(B₂O₅)₂O₁₆:Eu³⁺ (or Tb³⁺), Gd₂BaZnO₅:Eu³⁺ (or Tb³⁺),
 Gd₂O₂(SO₄):Eu³⁺ (or Tb³⁺), Gd₂P₄O₁₃:Eu³⁺ (or Tb³⁺), Gd₃O₄Br:Eu³⁺ (or Tb³⁺),
 Gd₃PO₇:Eu³⁺ (or Tb³⁺), Gd₃Te₂Li₃O₁₂:Eu³⁺ (or Tb³⁺), Gd₈P₂O₁₇:Eu³⁺ (or Tb³⁺), GdAl₃
 15 (BO₃)₄:Eu³⁺ (or Tb³⁺), GdAlO₃:Eu³⁺ (or Tb³⁺), GdAlO₃:Eu³⁺ (or Tb³⁺), GdB₃O₆:Eu³⁺ (or
 Tb³⁺), GdBO₃:Eu³⁺ (or Tb³⁺), GdGaO₃:Eu³⁺ (or Tb³⁺), GdOBr:Eu³⁺ (or Tb³⁺),
 GdOCl:Eu³⁺ (or Tb³⁺), GdP₃O₉:Eu³⁺ (or Tb³⁺), GdPO₄:Eu³⁺ (or Tb³⁺), I-CaB₂O₄:Eu³⁺ (or
 Tb³⁺), InBO₃:Eu³⁺ (or Tb³⁺), I-SrB₂O₄:Eu³⁺ (or Tb³⁺), KCaGd(PO₄)₂:Eu³⁺ (or Tb³⁺),
 La₂₆O₂₇(BO₃)₈:Eu³⁺ (or Tb³⁺), La₂BaZnO₅:Eu³⁺ (or Tb³⁺), La₂Hf₂O₇:Eu³⁺ (or Tb³⁺),
 20 La₂O₂(SO₄):Eu³⁺ (or Tb³⁺), La₂O₂S:Eu³⁺ (or Tb³⁺), La₂O₂S:Eu³⁺ (or Tb³⁺),
 La₂W₃O₁₂:Eu³⁺ (or Tb³⁺), La₂Zr₃(MoO₄)₉:Eu³⁺ (or Tb³⁺), La₃TaO₄Cl₆:Eu³⁺ (or Tb³⁺),
 La₃TaO₄Cl₆:Eu³⁺ (or Tb³⁺), La₃WO₆Cl₃:Eu³⁺ (or Tb³⁺), La₃WO₆Cl₃:Eu³⁺ (or Tb³⁺),
 LaAlO₃:Eu³⁺ (or Tb³⁺), LaAlO₃:Eu³⁺ (or Tb³⁺), LaB₃O₆:Eu³⁺ (or Tb³⁺), LaBO₃:Eu³⁺ (or
 Tb³⁺), LaF₃:Eu³⁺ (or Tb³⁺), LaF₃:Eu³⁺ (or Tb³⁺), LaGaO₃:Eu³⁺ (or Tb³⁺),
 25 LaMgB₅O₁₀:Eu³⁺ (or Tb³⁺), LaOBr:Eu³⁺ (or Tb³⁺), LaOCl:Eu³⁺ (or Tb³⁺), LaOF:Eu³⁺ (or
 Tb³⁺), LaOI:Eu³⁺ (or Tb³⁺), LaP₃O₉:Eu³⁺ (or Tb³⁺), LaPO₄:Eu³⁺ (or Tb³⁺), LaYO₃:Eu³⁺
 (or Tb³⁺), Li₂Lu₅O₄(BO₃)₃:Eu³⁺ (or Tb³⁺), Li₃Ba₂La₃(MoO₄)₈:Eu³⁺ (or Tb³⁺),
 Li₃La₂(BO₃)₃:Eu³⁺ (or Tb³⁺), Li₆Gd(BO₃)₃:Eu³⁺ (or Tb³⁺), Li₆Y(BO₃)₃:Eu³⁺ (or Tb³⁺),
 LiCaAlF₆:Eu³⁺ (or Tb³⁺), LiEu³⁺ (or Tb³⁺)Mo₂O₈:Eu³⁺ (or Tb³⁺), LiGd₆O₅(BO₃)₃:Eu³⁺
 30 (or Tb³⁺), LiGdF₄:Eu³⁺ (or Tb³⁺), LiGdGeO₄:Eu³⁺ (or Tb³⁺), LiGdO₂:Eu³⁺ (or Tb³⁺),
 LiGdSiO₄:Eu³⁺ (or Tb³⁺), LiLa₂O₂BO₃:Eu³⁺ (or Tb³⁺), LiLaGeO₄:Eu³⁺ (or Tb³⁺),

- LiLaO₂:Eu³⁺ (or Tb³⁺), LiLaP₄O₁₂:Eu³⁺ (or Tb³⁺), LiLaSiO₄:Eu³⁺ (or Tb³⁺),
 LiLuGeO₄:Eu³⁺ (or Tb³⁺), LiLuO₂:Eu³⁺ (or Tb³⁺), LiLuSiO₄:Eu³⁺ (or Tb³⁺), LiScO₂:Eu³⁺
 (or Tb³⁺), LiSr₂YO₄:Eu³⁺ (or Tb³⁺), LiSrAlF₆:Eu³⁺ (or Tb³⁺), LiSrAlF₆:Eu³⁺ (or Tb³⁺),
 LiY₆O₅(BO₃)₃:Eu³⁺ (or Tb³⁺), LiYF₄:Eu³⁺ (or Tb³⁺), LiYGeO₄:Eu³⁺ (or Tb³⁺),
 5 LiYO₂:Eu³⁺ (or Tb³⁺), LiYSiO₄:Eu³⁺ (or Tb³⁺), Lu₂O₂(SO₄):Eu³⁺ (or Tb³⁺),
 Lu₂Si₂O₇:Eu³⁺ (or Tb³⁺)₃ (or Tb³⁺), Lu₃Al₅O₁₂:Eu³⁺ (or Tb³⁺), Lu₃Al₅O₁₂:Yb:Eu³⁺ (or
 Tb³⁺), LuBO₃:Eu³⁺ (or Tb³⁺), LuBO₃ (calcite):Eu³⁺ (or Tb³⁺), LuOCl:Eu³⁺ (or Tb³⁺),
 LuPO₄:Eu³⁺ (or Tb³⁺), Mg₂Gd₈(SiO₄)₆O₂:Eu³⁺ (or Tb³⁺), Mg₂La₈(SiO₄)₆O₂:Eu³⁺ (or
 Tb³⁺), MgO:Eu³⁺ (or Tb³⁺), MgSiO₃:Eu³⁺ (or Tb³⁺), Na₃YSi₃O₉:Eu³⁺ (or Tb³⁺),
 10 Na₆Gd(BO₃)₃:Eu³⁺ (or Tb³⁺), NaGdGeO₄:Eu³⁺ (or Tb³⁺), NaGdO₂:Eu³⁺ (or Tb³⁺),
 NaGdSiO₄:Eu³⁺ (or Tb³⁺), NaGdSiO₄:Eu³⁺ (or Tb³⁺), NaLaGeO₄:Eu³⁺ (or Tb³⁺),
 NaLaO₂:Eu³⁺ (or Tb³⁺), NaLaSiO₄:Eu³⁺ (or Tb³⁺), NaLuGeO₄:Eu³⁺ (or Tb³⁺),
 NaLuSiO₄:Eu³⁺ (or Tb³⁺), NaScO₂:Eu³⁺ (or Tb³⁺), NaSrLa(VO₄)₂:Eu³⁺ (or Tb³⁺),
 NaYGeO₄:Eu³⁺ (or Tb³⁺), NaYSiO₄:Eu³⁺ (or Tb³⁺), ScBO₃:Eu³⁺ (or Tb³⁺), ScOCl:Eu³⁺ (or
 15 Tb³⁺), ScPO₄:Eu³⁺ (or Tb³⁺), Sr₂B₂O₅:Eu³⁺ (or Tb³⁺), Sr₂Gd₈(SiO₄)₆O₂:Eu³⁺ (or Tb³⁺),
 Sr₂La₂Zn₂O₇:Eu³⁺ (or Tb³⁺), Sr₂La₂Zn₂O₇:Eu³⁺ (or Tb³⁺), Sr₂LaAlO₅:Eu³⁺ (or Tb³⁺),
 Sr₃(BO₃)₂:Eu³⁺ (or Tb³⁺), Sr₃(PO₄)₂:Eu³⁺ (or Tb³⁺), Sr₃(PO₄)₂:Sm:Eu³⁺ (or Tb³⁺),
 Sr₃Gd₂(BO₃)₄:Eu³⁺ (or Tb³⁺), Sr₃La₂(BO₃)₄:Eu³⁺ (or Tb³⁺), Sr₃La₆(SiO₄)₆:Eu³⁺ (or
 Tb³⁺), Sr₃Y₂(BO₃)₄:Eu³⁺ (or Tb³⁺), Sr₅(PO₄)₃F:Eu³⁺ (or Tb³⁺), Sr₉Ln(VO₄)₇:Eu³⁺ (or
 20 Tb³⁺), SrAl₂B₂O₇:Eu³⁺ (or Tb³⁺), SrB₄O₇:Eu³⁺ (or Tb³⁺), SrB₆O₁₀:Eu³⁺ (or Tb³⁺),
 SrCO₃:Eu³⁺ (or Tb³⁺), SrGdAlO₄:Eu³⁺ (or Tb³⁺), SrHfO₃:Tm:Eu³⁺ (or Tb³⁺),
 SrLa₂BeO₅:(4c):Eu³⁺ (or Tb³⁺), SrLa₂BeO₅:(8d):Eu³⁺ (or Tb³⁺), SrLaAlO₄:Eu³⁺ (or Tb³⁺),
 SrLaGa₃O₇:Eu³⁺ (or Tb³⁺), SrLaO(BO₃):Eu³⁺ (or Tb³⁺), SrO:Eu³⁺ (or Tb³⁺), SrY₂O₄:(Sr-
 site):Eu³⁺ (or Tb³⁺), SrY₂O₄:(Y-site1):Eu³⁺ (or Tb³⁺), SrY₂O₄:(Y-site2):Eu³⁺ (or Tb³⁺),
 25 Tb₂Mo₃O₁₂:Eu³⁺ (or Tb³⁺), Tb₂W₃O₁₂:Eu³⁺ (or Tb³⁺), TbBO₃:Eu³⁺ (or Tb³⁺), ThO₂:Eu³⁺
 (or Tb³⁺), X1-Gd₂SiO₅:Eu³⁺ (or Tb³⁺), X1-Y₂SiO₅:Eu³⁺ (or Tb³⁺), X2-Y₂SiO₅:Eu³⁺ (or
 Tb³⁺), Y_{17.33}(BO₃)₄(B₂O₅)₂O₁₆:Eu³⁺ (or Tb³⁺), Y₂Ge₂O₇:Eu³⁺ (or Tb³⁺), Y₂GeO₅:Eu³⁺
 (or Tb³⁺), Y₂O₂(SO₄):Eu³⁺ (or Tb³⁺), Y₂O₂S:Eu³⁺ (or Tb³⁺), Y₂O₂S:Eu³⁺ (or Tb³⁺),
 Y₂O₃:Eu³⁺ (or Tb³⁺), Y₂P₄O₁₃:Eu³⁺ (or Tb³⁺), Y₂Si₂O₇:Eu³⁺ (or Tb³⁺), Y₂SiO₅:Eu³⁺ (or
 30 Tb³⁺), Y₃Al₅O₁₂:Eu³⁺ (or Tb³⁺), Y₃Ga₅O₁₂:Eu³⁺ (or Tb³⁺), Y₃O₄Br:Eu³⁺ (or Tb³⁺),
 Y₃O₄Cl:Eu³⁺ (or Tb³⁺), Y₃PO₇:Eu³⁺ (or Tb³⁺), Y₄GeO₈:Eu³⁺ (or Tb³⁺), Y₈P₂O₁₇:Eu³⁺

(or Tb³⁺), YAl₃(BO₃)₄:Eu³⁺ (or Tb³⁺), YAlO₃:Eu³⁺ (or Tb³⁺), YAlO₃:Eu³⁺ (or Tb³⁺), YBO₃:Eu³⁺ (or Tb³⁺), YbOBr:Yb:Eu³⁺ (or Tb³⁺), YF₃:Eu³⁺ (or Tb³⁺), YOBr:Eu³⁺ (or Tb³⁺), YOCl:Eu³⁺ (or Tb³⁺), YOCl:Eu³⁺ (or Tb³⁺), YOF:Eu³⁺ (or Tb³⁺), YOF:Eu³⁺ (or Tb³⁺), YP₃O₉:Eu³⁺ (or Tb³⁺), YPO₄:Eu³⁺ (or Tb³⁺), YPO₄:Eu³⁺ (or Tb³⁺), YT₂O₄:Eu³⁺ (or Tb³⁺), YVO₄:Eu³⁺ (or Tb³⁺), ZrP₂O₇:Eu³⁺ (or Tb³⁺), or mixtures thereof.

The skilled person will understand that the notation Eu³⁺ (or Tb³⁺) indicates that the host lattice is doped with Eu³⁺ or with Tb³⁺.

[0074] In an exemplary embodiment, the second luminescent material is selected from the group consisting of (Sr_n,Ca_{1-n})₁₀(PO₄)₆*B₂O₃:Eu²⁺ (wherein 0 ≤ n ≤ 1),
 10 (Ba,Sr,Ca)₅(PO₄)₃(Cl,F,Br,OH):Eu²⁺, (Ba,Sr,Ca)BPO₅:Eu²⁺, Sr₂Si₃O₈*2SrCl₂:Eu²⁺,
 (Ca,Sr,Ba)₃MgSi₂O₈:Eu²⁺, BaAl₈O₁₃:Eu²⁺, 2SrO*0.84P₂O₅*0.16B₂O₃:Eu²⁺,
 (Ba,Sr,Ca)MgAl₁₀O₁₇:Eu²⁺, (Ba,Sr,Ca)Al₂O₄:Eu²⁺, (Y,Gd,Lu,Sc,La)BO₃:Ce³⁺, Tb³⁺,
 (Ba,Sr,Ca)₂(Mg,Zn)Si₂O₇:Eu²⁺, (Mg,Ca,Sr,Ba,Zn)₂Si_{1-x}O_{4-2x}:Eu²⁺ (wherein 0 ≤ x ≤ 0.2),
 (Sr,Ca,Ba)(Al,Ga)₂S₄:Eu²⁺, (Ca,Sr)₈(Mg,Zn)(SiO₄)₄Cl₂:Eu²⁺, Na₂Gd₂B₂O₇:Ce³⁺, Tb³⁺,
 15 (Sr,Ca,Ba,Mg,Zn)₂P₂O₇:Eu²⁺, (Ca,Sr)S:Eu²⁺, Ce³⁺,
 (Y,Gd,Tb,La,Sm,Pr,Lu)₃(Sc,Al,Ga)_{5-n}O_{12-3/2n}:Ce³⁺ (wherein 0 ≤ n ≤ 0.5), (Y,Lu,Th)₃Al₅O₁₂:Ce³⁺,
 (Ca, Sr) Ga₂S₄:Eu²⁺, SrY₂S₄:Eu²⁺, CaLa₂S₄:Ce³⁺, (Ba,Sr,Ca)MgP₂O₇:Eu²⁺, CaWO₄,
 (Ba,Sr,Ca)_nSi_nN_n:Eu²⁺ (where 2n+4=3n), Ca₃(SiO₄)Cl₂:Eu²⁺, (Y,Lu,Gd)_{2-n}Ca_nSi₄N_{6+n}C_{1-n}:Ce³⁺,
 (wherein 0 ≤ n ≤ 0.5), (Lu,Ca,Li,Mg,Y) alpha-SiAlON doped with Eu²⁺ and/or Ce³⁺,
 20 (Ca,Sr,Ba)SiO₂N₂:Eu²⁺, Ce³⁺, (Sr,Ca)AlSiN₃:Eu²⁺, CaAlSi(ON)₃:Eu²⁺, Sr₁₀(PO₄)₆Cl₂:Eu²⁺,
 (BaSi)O₁₂N₂:Eu²⁺, SrSi₂(O,Cl)₂N₂:Eu²⁺, (Ba,Sr)Si₂(O,Cl)₂N₂:Eu²⁺ or mixtures thereof.

[0075] Preferably, the second luminescent material is excitable in the wavelength range between 380 to 580 nm. The second luminescent material may for instance be excitable in the UV-A (315 to 400 nm), violet (400 to 440 nm), blue (440 to 480 nm) or green (510 to 560 nm)
 25 wavelength range, preferably in the blue (440 to 480 nm) wavelength range. Preferably, the second luminescent material is doped with one or more ions selected from of the group consisting of Eu²⁺, Pb²⁺, Bi³⁺ and Ce³⁺, more preferably Ce³⁺ and Eu²⁺.

[0076] In a preferred embodiment, the second luminescent material is a Ce³⁺-doped garnet, such as Y₃Al₅O₁₂:Ce³⁺ ("YAG:Ce") or Lu₃Al₅O₁₂:Ce³⁺ ("LuAG:Ce") or a combination thereof.

[0077] Preferably, in the case of Ce^{3+} doping, the second luminescent material has a host lattice doped at a level of 0.05-5%, more preferably 0.1-4.

[0078] The mixture may comprise further luminescent materials. For instance, the mixture may comprise at least two emitting materials and/or at least two sensitizer materials. In a preferred embodiment, the mixture comprises first emitting material having a host lattice doped with Eu^{3+} ions; and a second emitting material having a host lattice doped with Tb^{3+} ions. The mixture may comprise a first sensitizer material and a second sensitizer material. The first sensitizer material and second sensitizer material may be so arranged to each other to allow energy transfer from the first sensitizer material to the first emitting material and/or from the second sensitizer material to the second emitting material.

[0079] It is possible to bring the first luminescent material (light emitting material) proximal to a large (e.g., several 10s, 100s, or 1000s nm) second luminescent material (sensitizer material). In this case, it may be beneficial to dope the donor sufficiently so that efficient non-radiative energy migration occurs between ions excited deep within the donor particle and those near the surface and which are thus likely to participate in FRET and give their energy to the neighboring first luminescent material. In the cases where high dopant concentrations lead to reduced quantum yields, for instance due to large size differences between the dopant atom in comparison to the target lattice site, co-doping with a second active ion can be used to enhance energy migration. It is important that FRET can occur between the first and second active ion within the same host lattice in order to have effective migration of the energy. In a preferred embodiment YAG: Ce^{3+} , LuAG: Ce^{3+} or a combination of these two materials are doped with <5% Ce^{3+} and co-doped with up to several 10's of percent Tb^{3+} . Energy migration might be beneficial for smaller particles as well, as well as helpful for the emitter particles.

25 *Second aspect of the invention*

[0080] In a second aspect of the invention, there is provided a method of treating a luminescent material comprising organic ligands, said method comprising:

- (a) removing at least part of said organic ligands from the luminescent material; and
- (b) after (a), annealing said luminescent material.

[0081] Said luminescent material comprising organic ligands may be any as described above. Preferably, the luminescent material is provided in the form of nanoparticles.

Third aspect of the invention.

- 5 [0082] The third aspect of the invention is directed to a method for preparing a luminescent composition, said method comprising:
- (i) providing a first luminescent material and a second luminescent material;
 - (ii) dispersing said first luminescent material and said second luminescent material in a liquid;
 - (iii) optionally, removing organic ligands from said first luminescent material and/or from said
10 second luminescent material;
 - (iv) removing said liquid, resulting in a dried product, wherein said removing comprises evaporation; and
 - (v) annealing said dried product.

15 *Removal of organic ligands in the second and third aspects of the invention*

[0083] The second aspect of the invention comprises removing at least part of said organic ligands. The third aspect of the invention optionally comprises removing organic ligands from the first luminescent material and/or from the second luminescent material. Removal of organic ligands is advantageous, since it enables efficient annealing without or with limited oxidation of organic
20 ligands.

[0084] Said removing at least part of said organic ligands may be effected by any method known in the art. For instance, organic ligand removal may be effected by contacting the luminescent material comprising organic ligands (or first luminescent material and/or the second luminescent material) with an acid, for instance HCl. The use of HCl to remove organic ligands is
25 described in *Wang et al, Tuning upconversion through Energy Migration in Core-Shell Nanoparticles, Supplementary Information, Nature Materials (2011) 1-35*. Another method is described in *Nano Lett., 2011, 11 (12), pp 5356–5361*.

[0085] Preferably, said removing at least part of said organic ligands is performed by the method of the first aspect of the invention.

Dispersing the luminescent material in a liquid;

5 [0086] Generally, the method according to the second aspect of the invention comprises dispersing the luminescent material in a liquid. The method according to the third aspect of the invention comprises dispersing the first luminescent material and the second luminescent material in a liquid.

10 [0087] Any suitable liquid may be used. The skilled person is able to select a preferred liquid considering the nature of the luminescent material (e.g. nanoparticles). In the event of a hydrophobic luminescent material (e.g. nanoparticles), a non-polar liquid is preferably used. In the event of a hydrophilic luminescent material (e.g. nanoparticles) a polar solvent is preferably used. Suitably the liquid comprises water or an alcohol (e.g. methanol or ethanol) or a mixture thereof.

15 [0088] In an embodiment, the liquid may be the solution comprising the oxidizing agent or a washing liquid which may be used to wash first luminescent material and the second luminescent material after an organic ligand removal step.

Removing said liquid, resulting in a dried product, wherein said removing comprises evaporation

20 [0089] The method according to the third aspect of the invention comprises removing the liquid, wherein the removing comprises evaporation. Generally, the method according to the second aspect of the invention comprises removing the liquid, wherein the removing comprises evaporation.

25 [0090] Removing the liquid by evaporation results in a dried product. Removing liquid by evaporation may be effected in any suitable manner, e.g. in an oven or under vacuum.

[0091] In the event the first luminescent material and second luminescent material are in the form of nanoparticles, the dried product is found to comprise clusters of nanoparticles.

In the dried product, the first luminescent material and second luminescent material are found to be in close proximity. In the embodiment wherein the first luminescent material and the second

luminescent material are selected such that the second luminescent material has an emission spectrum which overlaps at least partly with one or more of excitation bands of the first luminescent material, such close proximity enables non-radiative energy transfer between them.

5 *Annealing*

[0092] The methods according to the second, third and fourth aspects of the invention comprise annealing. Annealing can be effected in any suitable manner. Preferably, annealing is effected at a temperature of at least 200 °C, preferably at least 500 °C, such as between 200 and 1500 °C or 500 and 1600 °C, preferably between 300 and 1200 °C, or between 500 and 1300 °C.

10 Preferably, annealing is effected for a period of at least 30 seconds, preferably at least 1 minutes, more preferably from 1.5 minutes to 2 hours. Annealing may be effected for a period of at least 2 minutes, such as at least 5 minutes.

Shell growth – avoiding migration

15 [0093] It has been found that doping ions, for instance Ce ions, may be present at the surface of the particles or nanoparticles and that the annealing process according to the invention may result in migration of doping ions present in or at the surface of the first luminescent material into the second luminescent material. Likewise, it is found that doping ions present in or at the surface of the second luminescent material may undesirably migrate into the first luminescent material, and vice versa. This may lead to intermixed active ions, i.e. a co-doped system, which
20 may result in charge transfer quenching and lower luminescent efficiencies.

[0094] The inventors found how to avoid or at least mitigate this problem.

[0095] Preferably, (i) said first luminescent material is in the form of particles, preferably nanoparticles, wherein said first luminescent material comprises first doping ions, wherein said
25 particles comprise a core surrounded by a shell, and wherein the concentration of said first doping ions in said shell is lower than the concentration of said first doping ions in said core; and/or (ii) said second luminescent material is in the form of particles, preferably nanoparticles, wherein said second luminescent material comprises second doping ions, wherein said particles comprise a core surrounded by a shell, and wherein the concentration of said second doping ions in said shell is
30 lower than the concentration of said second doping ions in said core.

[0096] Preferably the methods according to the third and fourth aspects of the invention comprise (i) obtaining said first luminescent material by a method which comprises providing particles, preferably nanoparticles, doped with first doping ions, and growing a shell around said particles; and/or (ii) obtaining said second luminescent material by a method which comprises providing particles, preferably nanoparticles, doped with second doping ions, and growing a shell around said particles.

[0097] The shell of said particles of said first luminescent material may be free of said first doping ions and/or said shell of said particles of said second luminescent material may be free of said second doping ions. Preferably, the core and shell of the particles of the first luminescent material are comprised of the same host material and/or the core and the shell of the particles of the second luminescent material are comprised of the same host material.

[0098] By applying these preferred embodiments, surface ions doping ions that were initially sitting on the surface, may be surrounded by host material and no longer behave like (inactive or worse) surface ions. Furthermore, a non-doped shell around a doped core will act as diffusion buffer layer. When these nanocrystals are annealed at high temperature, ions can and will diffuse into this shell, but not into the other particles.

[0099] The shell thickness is preferably designed to be close to the diffusion length of ions at the annealing temperature and time, but not too thick as the sensitizer and emitter ions should be in close proximity to enable non-radiative inter-particle energy transfer. Therefore, preferred said shell of said particles of said first luminescent material has a thickness of between 2 and 10 nm, preferably between 3 and 5 nm and/or said shell of said particles of said second luminescent material has a thickness of between 2 and 10 nm, preferably between 3 and 5 nm.

[00100] In addition, the cores should preferably be as small as possible, to have a final core/shell particle size that still enables non-radiative inter-particle energy transfer. Therefore, preferably said core of said particles of said first luminescent material has a radius of less than 10 nm, preferably less than 5 nm; and/or said core of said particles of said second luminescent material has a radius of less than 10 nm, preferably less than 5 nm.

[00101] Furthermore, the core might have a very high doping concentration so that after annealing and diffusion, the complete particles have the final desired doping concentration.

[00102] It is also possible to grow a shell with doping ions that will not induce charge-transfer quenching with the emitter ions but which can act as migration ion. This would relax the requirements on the shell thickness, since a shell thicker than the diffusion length might still show energy transfer via the migration ion. E.g. having YAG:Ce,Tb as sensitizer, with an empty or Tb-doped shell mixed with YAG:Eu as emitter material.

[00103] Preferably, said first doping ions are selected from the group consisting of Eu^{3+} , Tb^{3+} , Mn^{4+} , preferably Eu^{3+} .

[00104] Preferably, said second doping ions are selected from the group consisting of Eu^{2+} , Pb^{2+} , Bi^{3+} and Ce^{3+} , preferably Ce^{3+} .

[00105] Preferably, said second luminescent material is $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ ("YAG:Ce") or $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ ("LuAG:Ce") or a combination thereof.

Procedure

[00106] Growing shells around nanoparticles is well known in the field of nanomaterials science. Seeded growth is an often used synthesis technique. Below, we give a concise background of the technique and theory behind it.

[00107] Seeded growth is a technique in which seeds (nanoscale materials, or porous bulk materials, or some hybrid of those two e.g. clustered nanocrystals) are added to a reaction mixture in which a material is grown. The surface of the seeds lowers the nucleation energy of the new material, promoting nucleation of the new material on the seeds. This is called heterogeneous nucleation. Heterogeneous nucleation will thus happen at lower temperatures and/or lower precursor concentrations than homogeneous nucleation, which allows to ultimately design a synthesis method that effectively suppresses homogeneous nucleation. The material that is grown on the seeds can be either the same material (homoepitaxial growth) or a different material (heteroepitaxial growth).

[00108] Different architectures are possible to obtain, e.g. core/shell geometries, segmented geometries, branched geometries, etc.

[00109] Different synthesis techniques can be employed in order to obtain the right balance between (heterogeneous) nucleation and growth:

- Seeded injection; in which the seeds are injected into a hot solution containing one (or more) of the precursors of the new material
 - Heating up; in which the seeds are added to a mixture of the precursors of the new material and everything is heated (slow or fast) to a desired reaction temperature.
- 5 - Dropwise addition; the precursors of the new material are added dropwise to a hot solution containing the seeds.
- Alternate addition; alternate addition of small amounts of two precursors (usually alternating between cation and anion), the so-called SILAR method. This addition can either be fast or slow (dropwise).
- 10 [00110] In heterogeneous catalysis a (slightly) comparable impregnation technique is often used, in which a porous support material is impregnated with a solution of (metal) precursor material that nucleates and grows into nano- or micro-sized particles upon heating. Note however, that these particles consist of only one element.
- [00111] Reference is made to: *Donega, Chem. Soc. Rev., 2011, 40, 1512–1546.*
- 15 [00112] Figs. 8-12 may help visualize the shell growth idea. Fig. 8 shows that upon annealing YAG:Ce nanoparticles, some clustering occurs. In Fig. 9, the ions diffuse from one particle to the other upon annealing, resulting in crystalline particles, however having inactive surface Ce and inactive particles as there's no inter-particle transfer.
- [00113] Fig. 10 visualizes how shells of YAG material are grown around YAG:Ce
- 20 nanoparticles, which upon annealing leads to less surface Ce (thus, more active ions), and less Ce(III) oxidation to Ce(IV). This can thus solve the problems of inactive Ce at the surface of particles. Further, as Figs. 11 and 12 help visualize, growing empty shells around the nanoparticles having a greater thickness than the diffusion length, allows the YAG:Ce and YAG:Eu to be annealed in the presence of each other.

25

First luminescent material and second luminescent material

[00114] The methods according to the third and fourth aspects of the invention comprises providing a first luminescent material and a second luminescent material.

[00115] Preferred characteristics and features of the first luminescent material and second luminescent material are the same as discussed in the first aspect of the invention. The first luminescent material and/or the second luminescent material may or may not comprise organic ligands.

5

Fourth aspect of the invention

[00116] The method according to the fourth aspect of the invention comprises:

- providing a composition comprising a first luminescent material and a second luminescent material, wherein said first luminescent material and said second luminescent material are selected such that said second luminescent material has an emission spectrum which overlaps at least partly with one or more excitation bands of said first luminescent material; and wherein said first luminescent material and said second luminescent material are so arranged to each other to allow non-radiative energy transfer from said second luminescent material to said first luminescent material; and
- annealing said composition.

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[00117] Surprisingly it is found that annealing of the composition enables to obtain a composition capable of providing increased non-radiative energy transfer.

[00118] The skilled person will understand that non-radiative energy transfer (sometimes also referred to as Fluorescent Resonance Energy Transfer, FRET) from the second luminescent material (or sensitizer material) to the first luminescent material (or light emitting material) involves the non-radiative transfer of energy from an excited sensitizer ion in the second luminescent material to an acceptor (or emitter) ion in the first luminescent material. It is evidenced and detectable by increased selective excitation of the sensitizer ion in the second luminescent material, resulting in increased emission from an emitter ion in the first luminescent material.

20

[00119] Detectable non-radiative energy transfer may be achieved in any suitable manner.

25

[00120] The skilled person will realize that – since resonant energy transfer is in first order inversely proportional to inter-ion distance at the power of 6 - the arrangement to allow non-radiative energy transfer may be effected by proper engineering of the effective distances between

the sensitizer ions in the sensitizer material and the emitter ions in the emitting material. It may for instance be achieved by the methods disclosed herein and/or by the topologies disclosed herein.

[00121] The composition comprising the first luminescent material and second luminescent material to be used in the method according to the fourth aspect of the invention may for instance
5 obtained or obtainable by applying the method according to steps (i), (ii), (iii) and (iv) of the third aspect of the invention. As discussed, this method enables to obtain the first luminescent material and second luminescent material in close enough proximity to allow non-radiative energy transfer between them.

[00122] The first luminescent material and the second luminescent material used in the
10 fourth aspect of the invention preferably have the characteristics as described in the discussion of the first aspect of the invention.

[00123] The luminescent composition may comprise further luminescent materials. For instance, the luminescent composition may comprise at least two emitting materials and/or at least two sensitizer materials. In a preferred embodiment, the luminescent material comprises a first
15 emitting material having a host lattice doped with Eu^{3+} ions; and a second emitting material having a host lattice doped with Tb^{3+} ions. The luminescent composition may comprise a first sensitizer material and a second sensitizer material. The first sensitizer material and second sensitizer material may be so arranged to each other to allow non-radiative energy transfer from the first sensitizer material to the first emitting material and/or from the second sensitizer material
20 to the second emitting material.

[00124] The composition used in the method according to the fourth aspect of the invention may be obtained in many different ways and may have a wide variety of forms.

[00125] According to a preferred embodiment of the fourth aspect of the invention, the first luminescent material and/or second luminescent material is provided as a nanophosphor.
25 According to the present invention, the term “nanophosphor” in the context of the present invention especially means and/or includes a topology in which at least one dimension thereof is in a nanometer scale, preferably $\leq 100\text{nm}$ or less. It should be noted that the first material together with the second material may comprise much larger structures.

[00126] Methods of producing such nanophosphors are inter alia described in *Development of nanophosphors-A review*, H. Chander, *Materials Science and Engineering*, **49**, 113-155 (2005).

[00127] The composition may be in the form of nanoparticles as discussed hereinabove.

5 [00128] According to a preferred embodiment of the fourth aspect of the invention the nanoparticles have a core-shell structure with undoped material forming the core and the first luminescent material forming a shell around the core. Advantages include to be able to lower the amount of the Eu^{3+} used and to increase overall energy transfer efficiency. If this embodiment is used, it is especially preferred that the thickness of the shell essentially made out of the first
10 luminescent material is ≥ 0.5 nm and ≤ 5 nm.

[00129] According to another preferred embodiment of the fourth aspect of the invention, the first luminescent material is provided, preferably essentially provided as a nanolayer, i.e. a layer in which the thickness of the layer is in a nanometer scale, preferably ≤ 100 nm or less, preferably ≥ 0.5 nm and ≤ 10 nm, whereas the width and breadth may be larger.

15 [00130] According to another preferred embodiment of the fourth aspect of the invention the second luminescent material is provided, preferably essentially provided as a nanophosphor (or nanoparticles), whereby *mutatis mutandis* and independently from the first material the above description can be applied here, too.

[00131] According to a further preferred embodiment of the fourth aspect of the invention,
20 the second luminescent material is provided, preferably essentially provided as a bulk material with the first material provided on the second luminescent material. In this context the term "bulk" especially means and/or includes greater than nano-scale, for example > 100 nm diameter and including micro-size scales.

[00132] According to a further embodiment of the fourth aspect of the invention the first
25 luminescent material and/or second luminescent material is provided, preferably essentially provided as a ceramic. The term "ceramic" according to the present invention refers to and/or encompasses in particular a compact crystalline or polycrystalline material which includes a controlled amount of pores or is non-porous. The term "polycrystalline material" according to the present invention refers to and/or encompasses in particular a material having a bulk density of
30 greater than 90 percent of the main component, consisting of more than 80 percent of individual

crystal domains, wherein each crystal domain has a diameter of 0.1 - 10 μm and a different crystallographic orientation. The individual crystal domains may be bonded to each other or diluted via an amorphous or glassy material or by additional crystalline phases. According to a preferred embodiment of the present invention the crystalline material has a density of $\geq 90\%$ to $\leq 100\%$ of the theoretical density. This has been found to be advantageous for many applications of the present invention.

[00133] According to a preferred embodiment of the fourth aspect of the invention, the first luminescent material and second luminescent material are provided, preferably essentially provided as several shells in a nanophosphor and/or nanoparticle material. In this regard several topologies are preferred within the present invention:

Core- shell- topologies

[00134] According to one embodiment, the first luminescent material forms the core whereas the second luminescent material is provided as a shell, according to an alternative the first luminescent material forms the shell whereas the second luminescent material forms the core. For both embodiments it is advantageous that both the core as well as the shell independently have a thickness of $\geq 1\text{nm}$ and $\leq 20\text{ nm}$.

Several shells

[00135] The above topology can be expanded to have a structure with several shells. Here the following structures have proven themselves to be especially of interest:

- First luminescent material as the core, second luminescent material around the core and a second layer of first luminescent material around the second luminescent material
- Second luminescent material as the core, first luminescent material around the core and a second layer of second luminescent material around the first luminescent material
- Undoped material as the core, second luminescent material around the core and a second layer of first luminescent material around the sensitizer material (or vice-a-versa)
- Four layer structures e.g. with an undoped core, then subsequently layers of first luminescent material, second luminescent material and first material around the core or

with an undoped core, then subsequently layers of second luminescent material, first luminescent material and second luminescent material around the core

For all these topologies it is preferred that independently from each other the thickness of each shell and/or the core is $\geq 0.5\text{nm}$ and $\leq 20\text{ nm}$.

5 [00136] Figure 13 shows – very schematically - a first embodiment of the composition which may be used in the fourth aspect of the present invention, in with both the first luminescent material 10 and the second luminescent material 20 are provided in the form of nanoparticles. As can be seen from Figure 13 the surface-to-surface distance between the particles is small enough to allow for direct non-radiative energy transfer from the second luminescent material 20 to the
10 first luminescent material 10. However, the undesired charge-transfer quenching usually does not or only seldom occur because here the distance between the second luminescent material and the Eu^{3+} of the first luminescent material is usually too large.

[00137] Figure 14 shows –very schematically - a second embodiment of the composition which may be used in the fourth aspect the present invention. In this embodiment, the second
15 luminescent material 20 is provided as a bulk material with the first luminescent material 10 provided as nanoparticles surrounding the second luminescent material. This approach has been shown to be especially promising if the emission of the sensitizer is also desired in the spectrum of the device, e.g., if the sensitizer material comprises YAG:Ce or the like.

[00138] Figures 15 to 18 show very schematical cross-sectional views through
20 nanoparticles according to the fifth to eight embodiments of the present invention.

[00139] In Figure 15 the nanoparticle has a core formed out of an undoped material 30 with the first luminescent material 10 forming a shell around it. It goes without saying that also an alternative embodiment where the second luminescent material forms the shell is an embodiment of the present invention.

25 [00140] In Figure 16 the second luminescent material 20 forms the core with the first luminescent material 10 provided as a shell around the core, in Fig. 17 it is the other way around i.e. the first luminescent material 10 forms the core, the second luminescent material 20 the shell.

[00141] The embodiment of Figure 18 shows a more complex structure with the first luminescent material 10 forming another shell around the particle of the embodiment of Fig. 17.
30 It goes without saying that also here the roles may be reversed (i.e. the second luminescent

material forming the core and the outer shell with the first luminescent material in between) or also topologies where undoped material is forming a shell or the core also are a part of the present invention.

[00142] It is possible to bring the first luminescent material (light emitting material) proximal to a large (e.g., several 10s, 100s, or 1000s nm) second luminescent material (sensitizer material). In this case, it may be beneficial to dope the donor sufficiently so that efficient non-radiative energy migration occurs between ions excited deep within the donor particle and those near the surface and which are thus likely to participate in FRET and give their energy to the neighboring Tb^{3+} and/or Eu^{3+} doped nanoparticles. In the case of YAG:Ce, wherein high ($> 3\%$) Ce^{3+} concentrations can lead to reduced quantum efficiencies due to the large Ce atom in comparison to the target lattice site, co-doping with Tb^{3+} (up to several 10's of percent) can be used to enhance energy migration. Energy migration might be beneficial for smaller particles as well, as well as helpful for the emitter particles.

[00143] Annealing of the composition can be effected in any suitable manner. Preferably, annealing is effected at a temperature of at least $200\text{ }^{\circ}\text{C}$, such as between 200 and $1500\text{ }^{\circ}\text{C}$, preferably between 300 and $1200\text{ }^{\circ}\text{C}$. Preferably, annealing is effected for a period of at least 5 minutes, more preferably from 15 minutes to 12 hours.

Luminescent material, light-emitting device and lighting system

[00144] The invention further relates to a luminescent material obtainable by any of the methods according to the invention.

[00145] In a preferred embodiment wherein the first luminescent material and the second luminescent material are selected such that the second luminescent material has an emission spectrum which overlaps at least partly with one or more of excitation bands of the first luminescent material, a luminescent material obtainable by the invention allows detectable energy transfer (FRET) from the second luminescent material (or sensitizer material) to the first luminescent material (light emitting material).

[00146] The skilled person will understand that non-radiative energy transfer (sometimes also referred to as Fluorescent Resonance Energy Transfer, FRET) from the second luminescent material (or sensitizer material) to the first luminescent material (or light emitting material)

involves the non-radiative energy transfer of energy from an excited sensitizer ion in the second luminescent material to an acceptor (or emitter) ion in the first luminescent material. It is evidenced and detectable by increased selective excitation of the sensitizer ion in the second luminescent material, resulting in increased emission from an emitter ion in the first luminescent material.

5 **[00147]** The invention further relates to a light-emitting device comprising the luminescent material obtainable by the method according to the invention. Preferably the light-emitting device further comprises an excitation source for the luminescent material, such as for the second luminescent material. Preferably the excitation sources is a UV-A, violet or blue light emitting material which emits light towards the luminescent material with a wavelength of 315-400 nm
10 (UV-A), 400-440 nm (violet) or 440-480 nm (blue), more preferably between 430-465 nm.

[00148] The invention further relates to a lighting system comprising a light emitting device according to the invention. Preferably, the lighting system is selected from the group consisting of a lamp or luminaire, office lighting systems, household application systems shop lighting systems, home lighting systems, accent lighting systems, spot lighting systems, theater lighting systems,
15 fiber-optics application systems, projection systems, self-lit display systems, pixelated display systems, segmented display systems, warning sign systems, medical lighting application systems, indicator sign systems, and decorative lighting systems, portable systems, automotive applications and green house lighting systems.

[00149] The invention will now further be illustrated using the following examples, without
20 however being limited thereto.

EXAMPLES

Example 1: Exemplary Procedure

25 **[00150]** The following exemplary procedure is provided:

- Nanomaterials are mixed together in the desired weight ratios. This could be either in dried (powder) form, or dispersed in a liquid.
- A solvent is added; typically 5-20 mL of either water, methanol or ethanol is added to 100-200 mg of nanomaterials.
- 30 - Mixture is shaken and stirred for a few minutes

- Mixture is sonicated for 1.5 hrs
- Base piranha solution is prepared in the meantime: concentrated NH_4OH solution (30% in water) is heated to 60°C, the H_2O_2 (30% in water) is added in a ~3:1 ratio and reheated to 60°C.
- 5 - About 15 mL of the base piranha solution is added to the nanopowder dispersion/solution and heated to 60-80°C and stirred for 90 min.
- After 30 min. solution/dispersion was cooled to room temperature and centrifuged at 3000 rpm for 10 min
- 10 - Piranha solution was removed after centrifuging, and 5 mL of acidic ethanol was added to wash (pH 4, prepared by adding 0.1M HCl to ethanol). Mixture was shaken and sonicated for a few minutes to disperse the materials again.
- Centrifuged again (3000 rpm, 10 min), removed supernatant and re-mixed in acidic ethanol.
- 15 - In total particles were washed 5 times with acidic ethanol before adding few mL water
- Particles were dried in the oven at 120-180 °C.
- Sample was grinded into a powder

Example 2: Ligand removal from $\text{LaPO}_4:\text{Eu}^{3+}$ (10%) + $\text{LaPO}_4:\text{Tb}^{3+}$ (40%) nanoparticles

[00151] $\text{LaPO}_4:\text{Eu}^{3+}$ (5%) + $\text{LaPO}_4:\text{Tb}^{3+}$ (40%) nanoparticles with tributylamine ligands were synthesized using the following (known in literature) procedure:

A typical recipe for the preparation of $\text{La}_{1-x}\text{Ln}_x\text{PO}_4$ nanoparticles in a high boiling coordinating solvent is as follows:

- 25 • Dissolve a total of 10 mmol $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$, with a ratio depending on the desired doping level, in approximately 10 mL of methanol p.a. in a 100 mL 3-neck round-bottomed flask and acquire a clear solution
- Add 10.9 mL, 10.650 g (40 mmol) tributyl phosphate
- Remove methanol from solution under vacuum (Schlenk-line), careful with vacuum

- Add 30 mL (32 g) diphenyl ether
- Open system, flush afterwards
- Remove the water released by the hydrated metal chlorides under vacuum at 105°C (Schlenk line) – water should evaporate around 80-85°C
- 5 • Cool down reaction mixture to below 50°C and add 9.5 mL, 7.41 g (40 mmol) tributylamine to the clear solution (under nitrogen)
- Add 7.0 mL of a 2 M solution phosphoric acid in dihexyl ether (dissolve 1.96 g H₃PO₄ in 10 mL dihexyl ether under ultrasonification), large vial
- Heat the mixture to 200°C for 16 hours and cool reaction mixture to room temperature
- 10 • Separate nanocrystals by centrifuging at 2000 rpm for 5 minutes
- Wash nanocrystals several times with toluene, careful with adding methanol
- Dry powder under vacuum
- The powder should be redispersible in methanol
- Perform S-ray Diffraction (XRD) measurements to determine whether the La_{1-x}PO₄:Ln_x
- 15 is obtained

[00152] The procedure described in example 1 was followed. The nanoparticles were mixed in a 1:1 weight ratio.

FTIR spectra of the LaPO₄ particles before and after ligand removal were measured. The results have been indicated in Figure 1. In this figure peaks around 1450 and 2950 cm⁻¹ indicate C-H
20 bending and stretching from the ligands respectively, which are clearly present in the case of the sample measured before ligand removal. After the ligand removal treatment these peaks are no longer present, indicating that ligands have been successfully removed.

Example 3: Evidence for energy transfer

25 [00153] In this example the following experiments are performed to show the occurrence of energy transfer in the LaPO₄ particles obtained in example 2.

[00154] To this end the behavior of the LaPO₄ particles obtained in example 2 is compared to that of LaPO₄:Eu (10%) + LaPO₄:Tb (40%) nanoparticles (also in a 1:1 weight ratio) which do not exhibit energy transfer, as the LaPO₄:Eu (10%) nanoparticles and LaPO₄:Tb (40%)
30 nanoparticles are processed separately by the following “dry mixing” process

- Nanomaterials of interest are weighted in the desired weight ratios, but both put into a different vial (not mixed together). This could be either in dried (powder) form, or dissolved/dispersed in a liquid.
 - A solvent is added in both vials; typically 5-20 mL of either water, methanol or ethanol is added to 100-200 mg of nanomaterials.
 - Dispersions are shaken and stirred for a few minutes
 - Dispersions are sonicated for 1.5 hrs
 - Base piranha solution is prepared in the meantime: concentrated NH_4OH solution (30% in water) is heated to 60C, the H_2O_2 (30% in water) is added in a ~3:1 ratio and reheated to 60C.
 - About 15mL of the base piranha solution is added to the nanopowder dispersions/solutions and heated to 60-80C and stirred for 90 min.
 - After 30 min. solutions/dispersions were cooled to room temperature and centrifuged at 3000 rpm for 10 min
 - Piranha solution was removed after centrifuging, and 5 mL of acidic ethanol was added to wash (pH 4, prepared by adding 0.1M HCl to ethanol). Samples were shaken and sonicated for a few minutes to disperse the materials again.
 - Centrifuged again (3000 rpm, 10 min), removed supernatant and re-mixed in acidic ethanol.
 - In total particles were washed 5 times with acidic ethanol before adding few mL water
 - Particles were dried in the oven at 120-180C.
 - Materials were grinded into a powder.
 - Materials were put together and mixed by shaking the bottle
- 25 **[00155]** Then, the following measurements were performed on both samples (i.e. the sample obtained in example 2 and the sample obtained by the dry mixing)
- Samples were excited at 484.5 nm, were only Tb is excitable. Figure 2 shows the emission intensity from 670-720 nm, were only Eu^{3+} emits light. Clearly, the

sample obtained in example 2 shows much more emission in this region, indicating energy transfer from Tb $\rightarrow$ Eu.

- Samples were excited at 395 nm, where only Eu³⁺ is excitable and no IFRET processes can take place. Figure 3 shows that both the sample according to example 2 and 'dry mixed' samples show very similar (Eu³⁺) emission intensities, indicating that in both mixtures the Eu³⁺ has very similar activity.
- Excitation spectrum was recorded of the Eu³⁺ emission at 695 nm, shown in Fig. 4. Only for the sample obtained in example 2 the Tb excitation lines are clearly visible, indicating IFRET mechanisms.
- Figure 5 shows the decay of both samples, which is clearly accelerated in case of the sample obtained in example 2, which is a typical signature of non-radiative energy transfer processes.

Example 4

[00156] Four different methods were used to treat the nanoparticles:

1. HCl treatment (as in Wang et al, Tuning upconversion through Energy Migration in Core-Shell Nanoparticles, Supplementary Information, Nature Materials (2011) 1-35). This method did not work in our case (see Table 1), and strong acids can damage or even dissolve the nanoparticles.
2. (NH₄)₂S treatment, which is an example of a more selective method: This procedure is based on Nano Lett., 2011, 11 (12), pp 5356-5361, where they show ligand removal of InP and CdSe quantum dots, while maintaining quantum confinement. They also show that the particles touch after ligand removal and do not touch before ligand removal. The principle is that S binds to the metal of the nanoparticle host lattice, while (NH₄) binds to the oleic acid ligand, thereby decoupling the nanoparticles from the ligands. This method works for some nanoparticle-ligand couples, but is much more selective than treatment by an oxidizing agent (see Table 1)

- 0.004 M (NH₄)₂S solution was prepared by adding 0.03 mL 50 w% (NH₄)₂S solution in water to 50 mL methanol.
- 10 mL of this solution was added to ~200g nanoparticles, and stirred for 15 minutes

- Acetone was added to sediment the particles, and the mixture was centrifuged (10 min. @3000 rpm)
- Supernatant was removed, and acidic ethanol was added (pH 4, prepared by adding 0.1M HCl to ethanol). Mixture was shaken and sonicated for 40 min.
- 5 - Particles were washed 4 times with acidic ethanol before adding few mL water.
- The LaPO₄:Ce particles were washed again 4 times with water. The YVPO₄:Eu didn't come out of solution after adding water, so no further washing was done.
- Particles were dried in the oven at 180-200C.

In our case we found successful ligand removal in some, but not all cases for this method.

- 10 3. Thermal treatment: a few hours at 1100C in air
4. Base piranha treatment as described above.

After treatment the samples were measured using FTIR, or put in the oven at 300C (in air) for 2 hours. In case organic ligands are present, they will turn black which is clearly visible by eye. If
15 organic ligands have successfully been removed, the material will not change color or become a lighter color.

Table 1

Material	Ligand	Method	Ligands removed?
LaPO ₄ :Ce (~4 nm diameter)	tributylamine	(NH ₄) ₂ S treatment (literature)	Yes
LaPO ₄ :Ce (~4 nm diameter)	tributylamine	Base piranha treatment	Yes
LaPO ₄ :Ce (~4 nm diameter)	Tributylamine	Thermal treatment (1100C)	Yes, but Ce ⁴⁺ formation
YVPO ₄ :Eu (~7 nm diameter)	Ethylene glycol	(NH ₄) ₂ S treatment (literature)	No
YVPO ₄ :Eu (~7 nm diameter)	Ethylene glycol	Base piranha treatment	Yes
YVPO ₄ :Eu (~7 nm diameter)	Ethylene glycol	Thermal treatment (1100C)	Yes
Y ₃ Al ₅ O ₁₂ :Ce (~7 nm diameter)	Ethylene glycol	Base piranha	Yes
NaYF ₄ :Eu (~20 nm diameter)	Oleate	HCl treatment	No
NaYF ₄ :Eu (~20 nm diameter)	Oleate	(NH ₄) ₂ S treatment (literature)	Yes
NaYF ₄ :Eu (~20 nm diameter)	Oleate	Base piranha treatment	Yes

Example 5: Exemplary Procedure

[00157] The following exemplary procedure is provided:

- Nanomaterials are mixed together in the desired weight ratios. This could be either in dried (powder) form, or dissolved/dispersed in a liquid.
- A solvent is added; typically 5-20 mL of either water, methanol or ethanol is added to 100-200 mg of nanomaterials.
- Mixture is shaken and stirred for a few minutes
- Mixture is sonicated for 1.5 hrs
- Base piranha solution is prepared in the meantime: concentrated NH_4OH solution (30% in water) is heated to 60C, the H_2O_2 (30% in water) is added in a ~3:1 ratio and reheated to 60C.
- About 15mL of the base piranha solution is added to the nanopowder dispersion/solution and heated to 60-80 C and stirred for 90 min.
- After 30 min. solution/dispersion was cooled to room temperature and centrifuged at 3000 rpm for 10 min
- Piranha solution was removed after centrifuging, and 5 mL of acidic ethanol was added to wash (pH 4, prepared by adding 0.1M HCl to ethanol). Mixture was shaken and sonicated for a few minutes to disperse the materials again.
- Centrifuged again (3000 rpm, 10 min), removed supernatant and re-mixed in acidic ethanol.
- In total particles were washed 5 times with acidic ethanol before adding few mL water
- Particles were dried in the oven at 120-180C.
- Sample was grinded into a powder

Example 6 (with annealing) and Example 7 (without annealing)

[00158] $\text{LaPO}_4:\text{Eu}^{3+}$ (5%) + $\text{LaPO}_4:\text{Tb}^{3+}$ (40%) nanoparticles with tributylamine ligands were synthesized using the following (known in literature) procedure:

A typical recipe for the preparation of $\text{La}_{1-x}\text{Ln}_x\text{PO}_4$ nanoparticles in a high boiling coordinating solvent is as follows:

- Dissolve a total of 10 mmol $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$, with a ratio depending on the desired doping level, in approximately 10 mL of methanol p.a. in a 100 mL 3-neck round-bottomed flask and acquire a clear solution
- Add 10.9 mL, 10.650 g (40 mmol) tributyl phosphate
- 5 • Remove methanol from solution under vacuum (Schlenk-line), careful with vacuum
- Add 30 mL (32 g) diphenyl ether
- Open system, flush afterwards
- Remove the water released by the hydrated metal chlorides under vacuum at 105°C (Schlenk line) – water should evaporate around 80-85°C
- 10 • Cool down reaction mixture to below 50°C and add 9.5 mL, 7.41 g (40 mmol) tributylamine to the clear solution (under nitrogen)
- Add 7.0 mL of a 2 M solution phosphoric acid in dihexyl ether (dissolve 1.96 g H_3PO_4 in 10 mL dihexyl ether under ultrasonification), large vial
- Heat the mixture to 200°C for 16 hours and cool reaction mixture to room temperature
- 15 • Separate nanocrystals by centrifuging at 2000 rpm for 5 minutes
- Wash nanocrystals several times with toluene, careful with adding methanol
- Dry powder under vacuum
- The powder should be redispersible in methanol
- Perform S-ray Diffraction (XRD) measurements to determine whether the $\text{La}_{1-x}\text{PO}_4:\text{Ln}_x$
- 20 is obtained

[00159] The procedure described in example 1 was followed. The nanoparticles were mixed in a 1:1 weight ratio.

[00160] In example 2 the sample (grinded powder) was annealed at 600 °C for 2 hrs before measuring the spectra.

25 [00161] In example 3 the sample (grinded powder) this annealing step was not applied.

[00162] Both samples are excited in the Tb^{3+} at 484.5 nm, with the same intensity and measured at room temperature. The sample “After annealing” (example 2) clearly shows a factor more than 2 stronger Eu^{3+} emission compared to the sample “Before annealing” (example 3), see Figure 6. Surprisingly, the sample does not only show a higher overall emission intensity, but also

a high IFRET efficiency as can be seen from Figure 7. In Figure 7 the excitation spectrum of Eu^{3+} is measured at 697 nm, where the Tb excitation lines are clearly relatively more intense after annealing compared to before. This indicates a higher IFRET efficiency.

CLAIMS

1. Method for treating a luminescent material comprising organic ligands, said method comprising
- 5 contacting said luminescent material comprising organic ligands with an oxidizing agent.
2. Method according to claim 1, wherein said luminescent material is in the form of nanoparticles, preferably wherein the D_{50} value of the nanoparticles is $\geq 1\text{nm}$ and $\leq 100\text{nm}$.
3. Method according to any preceding claim, wherein said oxidizing agent comprises H_2O_2 .
- 10 4. Method according to any preceding claim, further comprising separating said luminescent material from the oxidizing agent.
5. Method according to any preceding claim, wherein said contacting is carried out in the presence of a solution comprising the oxidizing agent, preferably wherein said solution comprises water or an alcohol (e.g. methanol or ethanol) or a mixture thereof.
- 15 6. Method according to claim 5, wherein said solution comprises NH_4OH .
7. Method according to claim 5 or 6, further comprising recovering said luminescent material from said solution.
8. Method according to claim 7, wherein said recovering said luminescent material from the solution comprises gravity separation (preferably centrifugation) and/or drying by
- 20 evaporation.
9. Method according to claim 8 or 9, wherein said recovering said luminescent material from the solution comprises washing said luminescent material using a washing liquid and recovering said luminescent material from said washing liquid, preferably wherein said recovering said luminescent material from said washing liquid comprises gravity separation
- 25 (preferably by centrifugation) and/or drying by evaporation.
10. Method according to any preceding claim, wherein said luminescent material comprising organic ligands is a mixture comprising at least a first luminescent material and a second luminescent material, and wherein the first luminescent material and/or second luminescent material comprise organic ligands, preferably wherein the first luminescent material and the
- 30 second luminescent material comprise organic ligands.

11. Method for treating a luminescent material comprising organic ligands, said method comprising:
- (a) removing at least part of said organic ligands from the luminescent material; and
 - (b) after (a), annealing said luminescent material.
- 5 12. Method according to claim 11, wherein said luminescent material is in the form of nanoparticles, preferably wherein the D_{50} value of the nanoparticles is $\geq 1\text{nm}$ and $\leq 100\text{nm}$.
13. Method for preparing a luminescent composition, said method comprising:
- (i) providing a first luminescent material and a second luminescent material;
 - 10 (ii) dispersing said first luminescent material and said second luminescent material in a liquid;
 - (iii) optionally, removing organic ligands from said first luminescent material and/or from said second luminescent material;
 - (iv) removing said liquid, resulting in a dried product, wherein said removing comprises
 - 15 evaporation; and
 - (v) annealing said dried product.
14. Method according to any one of claims 10 or 13, wherein said first luminescent material and said second luminescent material are selected such that said second luminescent material has an emission spectrum which overlaps at least partly with one or more of
- 20 excitation bands of the first luminescent material.
15. Method according to any one of claim 10 or 13-14, wherein said first luminescent material and/or said second luminescent material are in the form of nanoparticles, preferably wherein said first luminescent material and said second luminescent material are in the form of nanoparticles, preferably wherein the D_{50} value of the nanoparticles is $\geq 1\text{nm}$ and $\leq$
- 25 100 nm.
16. Method, for instance according to any one of claims 13-15, for preparing a luminescent composition, said method comprising:
- providing a composition comprising a first luminescent material and a second luminescent material, wherein said first luminescent material and said second
 - 30 luminescent material are selected such that said second luminescent material has an emission spectrum which overlaps at least partly with one or more of excitation bands

of said first luminescent material; and wherein said first luminescent material and said second luminescent material are so arranged to each other to allow non-radiative energy transfer from said second luminescent material to said first luminescent material; and

- 5 - annealing said composition.
17. Method according to any one of claims 10 or 13-16, wherein said first luminescent material is a red emitting material.
18. Method according to any one of claims 10 or 13-17, wherein said first luminescent material is doped with one or more ions selected from the group consisting of Eu^{3+} , Tb^{3+} , Mn^{4+} .
- 10 19. Method according to any one of claims 10 or 13-18, wherein said second luminescent material is excitable in the wavelength range between 380 to 580 nm, preferably wherein said second luminescent material is excitable in the UV-A (315 to 400 nm), violet (400 to 440 nm), blue (440 to 480 nm) or green (510 to 560 nm) wavelength range, preferably in the blue (440 to 480 nm) wavelength range.
- 15 20. Method according to any one of claims 10 or 13-19, wherein said second luminescent material is doped with one or more ions selected from the group consisting of Eu^{2+} , Pb^{2+} , Bi^{3+} and Ce^{3+} .
21. Method according to any one of claims 10 or 13-20, wherein said second luminescent material is $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ ("YAG:Ce") or $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ ("LuAG:Ce") or a combination thereof.
- 20 22. Method according to any of claims 11-21, wherein said annealing is effected at a temperature of between 200 and 1500 °C.
23. Method according to any one of claims 13-22, wherein said liquid comprises water or an alcohol (e.g. selected from the group consisting of methanol, ethanol, isopropanol or mixtures thereof) or a mixture thereof.
- 25 24. Method according to any one of claims 13-22, wherein (iii) is not optional, preferably wherein the method comprises removing organic ligands from said first luminescent material and from said second luminescent material.
25. Method according to claim 24, wherein said removing organic ligands comprises
- 30 contacting said first luminescent material and/or said second luminescent material with an oxidizing agent, preferably in the presence of a solution comprising said oxidizing agent.

26. Method according to any one of claims 10 or 13-25, wherein
- (i) said first luminescent material is in the form of particles, preferably nanoparticles, wherein said first luminescent material comprises first doping ions, wherein said particles comprise a core surrounded by a shell, and wherein the concentration of said first doping ions in said shell is lower than the concentration of said first doping ions in said core; and/or
- (ii) said second luminescent material is in the form of particles, preferably nanoparticles, wherein said second luminescent material comprises second doping ions, wherein said particles comprise a core surrounded by a shell, and wherein the concentration of said second doping ions in said shell is lower than the concentration of said second doping ions in said core.
27. Method according to any one of claims 10 or 13-26, further comprising
- (i) obtaining said first luminescent material by a method which comprises providing particles, preferably nanoparticles, doped with first doping ions, and growing a shell around said particles; and/or
- (ii) obtaining said second luminescent material by a method which comprises providing particles, preferably nanoparticles, doped with second doping ions, and growing a shell around said particles
28. Method according to claim 26 or 27, wherein said shell of said particles of said first luminescent material is free of said first doping ions and/or wherein said shell of said particles of said second luminescent material is free of said second doping ions.
29. Method according to any one of claims 26-28, wherein said shell of said particles of said first luminescent material has a thickness of between 2 and 6 nm, preferably between 3 and 5 nm and/or wherein said shell of said particles of said second luminescent material has a thickness of between 2 and 6 nm, preferably between 3 and 5 nm.
30. Method according to any one of claims 26 to 29, wherein said core of said particles of said first luminescent material has a diameter of less than 4 nm, preferably less than 3 nm; and/or wherein said core of said particles of said second luminescent material has a diameter of less than 4 nm, preferably less than 3 nm.
31. Method according to any one of claims 26 to 30, wherein said first doping ions are selected from the group consisting of Eu^{3+} , Tb^{3+} , Mn^{4+} , preferably Eu^{3+} .

32. Method according to any one of claims 26 to 31, wherein said second doping ions are selected from the group consisting of Eu^{2+} , Pb^{2+} , Bi^{3+} and Ce^{3+} , preferably Ce^{3+} .
33. Method according to any one of claims 26 to 32, wherein said second luminescent material is $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ ("YAG:Ce") or $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ ("LuAG:Ce") or a combination thereof.
- 5 34. Method according to any one of claims 26 to 33, wherein the core and shell of the particles of the first luminescent material are comprised of the same host material and/or wherein the core and the shell of the particles of the second luminescent material are comprised of the same host material.
35. Luminescent material or luminescent composition obtainable by the method according to
10 any one preceding claim.
36. Luminescent material obtainable by the method according to claim 35, wherein said luminescent material allows non-radiative energy transfer from said second luminescent material to said first luminescent material.
37. Light-emitting device, said light emitting device comprising the luminescent material
15 according to claim 35 or 36, preferably wherein light-emitting device further comprises an excitation source for the luminescent material, such as for the second luminescent material.
38. A lighting system comprising a light emitting device according to claim 37, preferably, wherein the lighting system is selected from the group consisting of a lamp or luminaire, office lighting systems, household application systems shop lighting systems, home
20 lighting systems, accent lighting systems, spot lighting systems, theater lighting systems, fiber-optics application systems, projection systems, self-lit display systems, pixelated display systems, segmented display systems, warning sign systems, medical lighting application systems, indicator sign systems, and decorative lighting systems, portable systems, automotive applications and green house lighting systems.
- 25

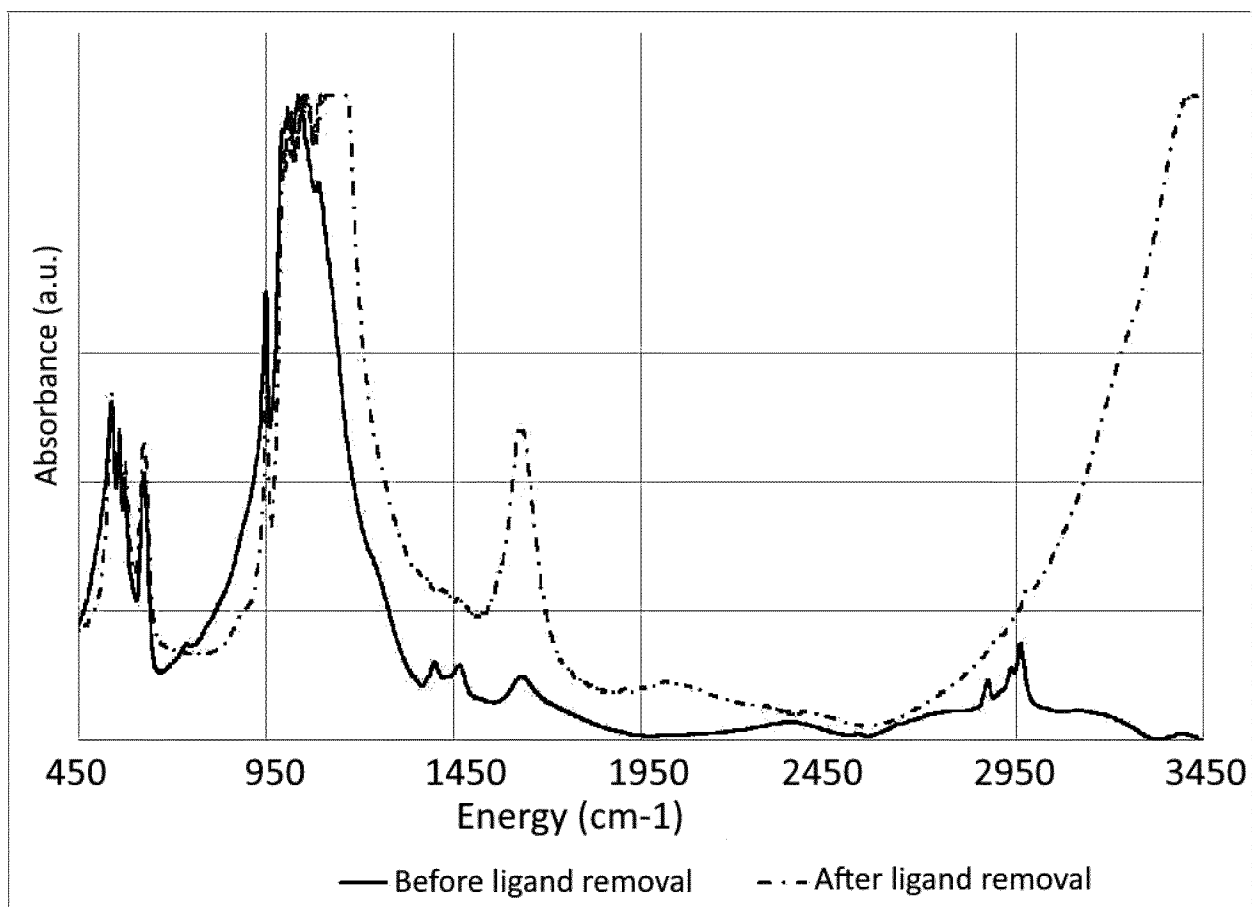
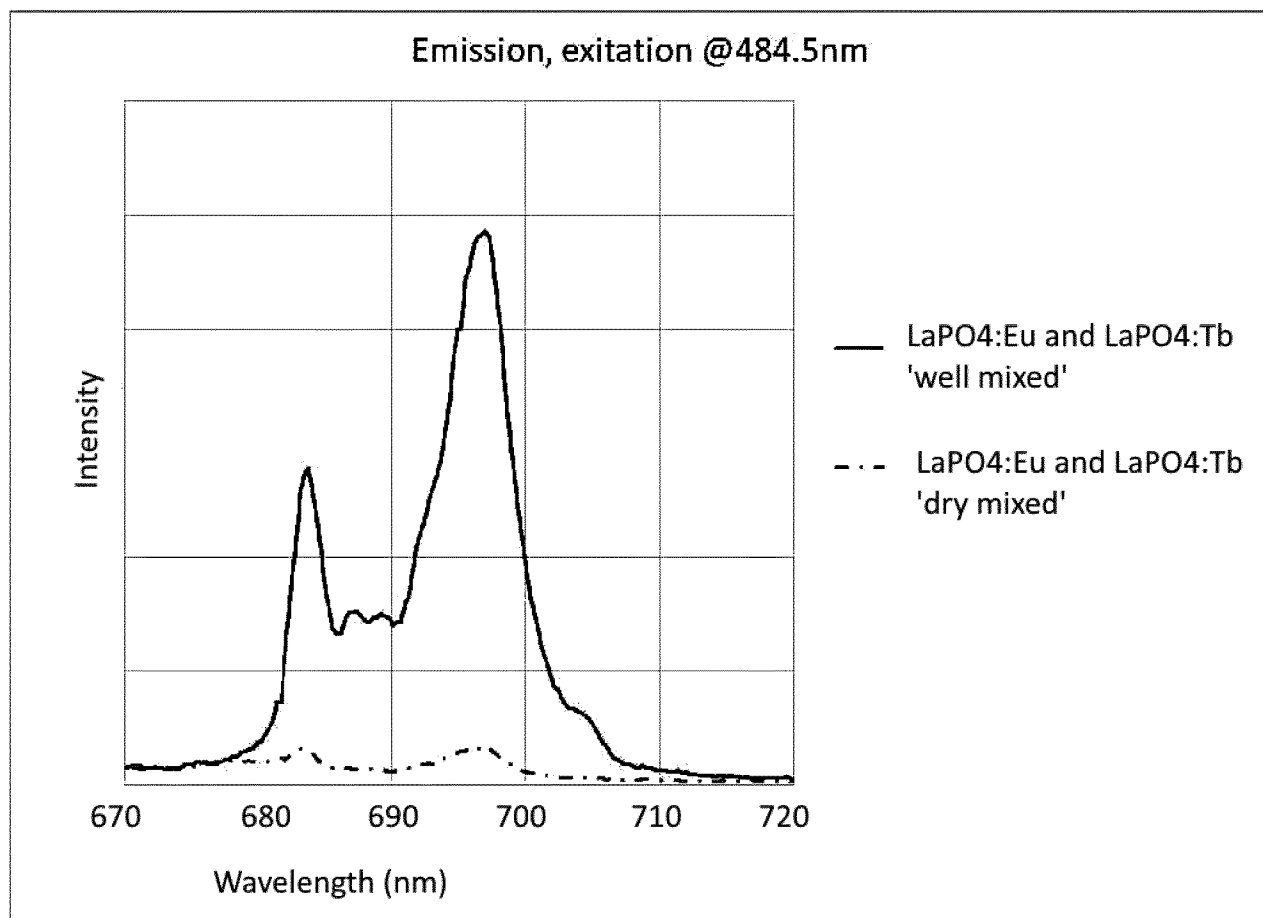


FIGURE 1

FIGURE 2



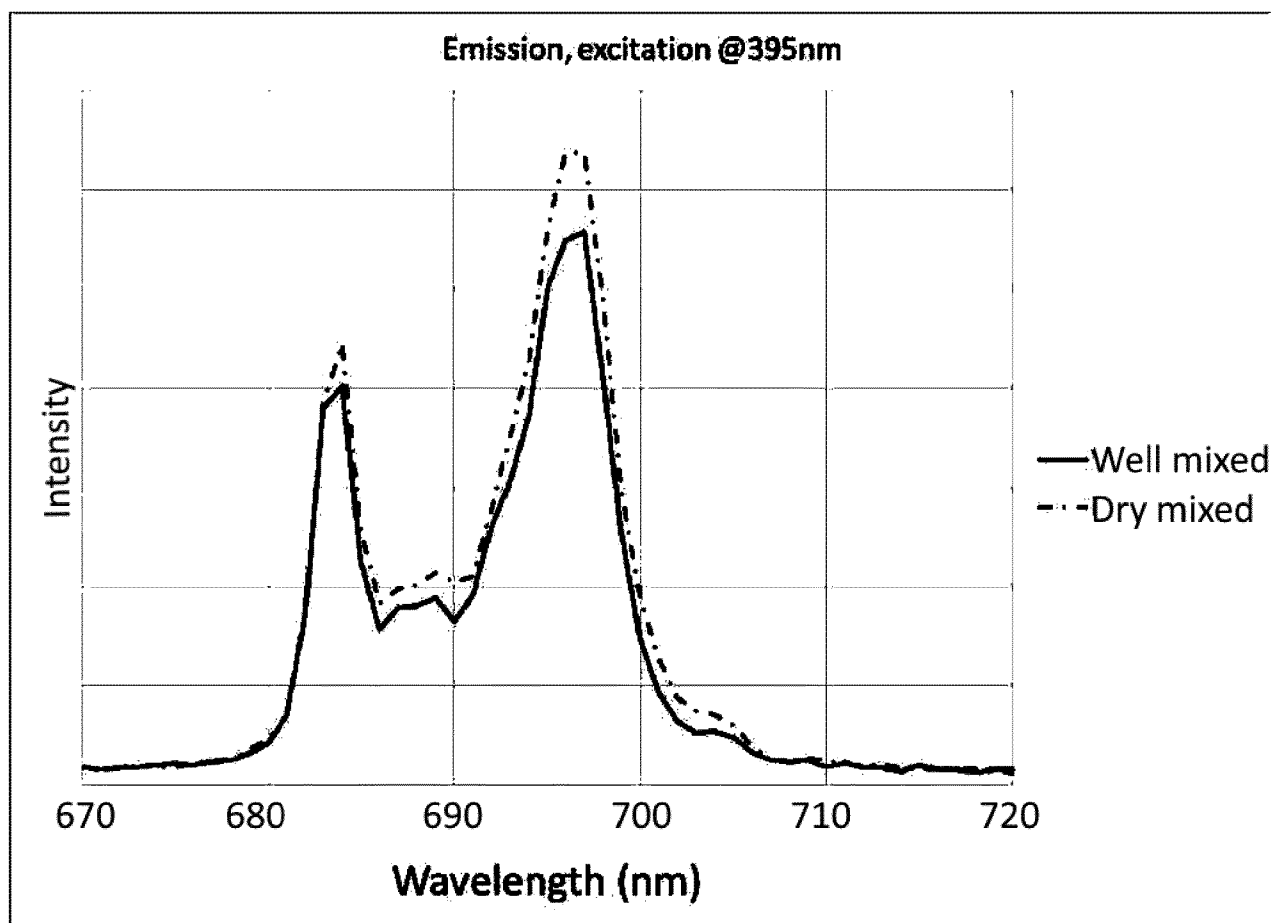
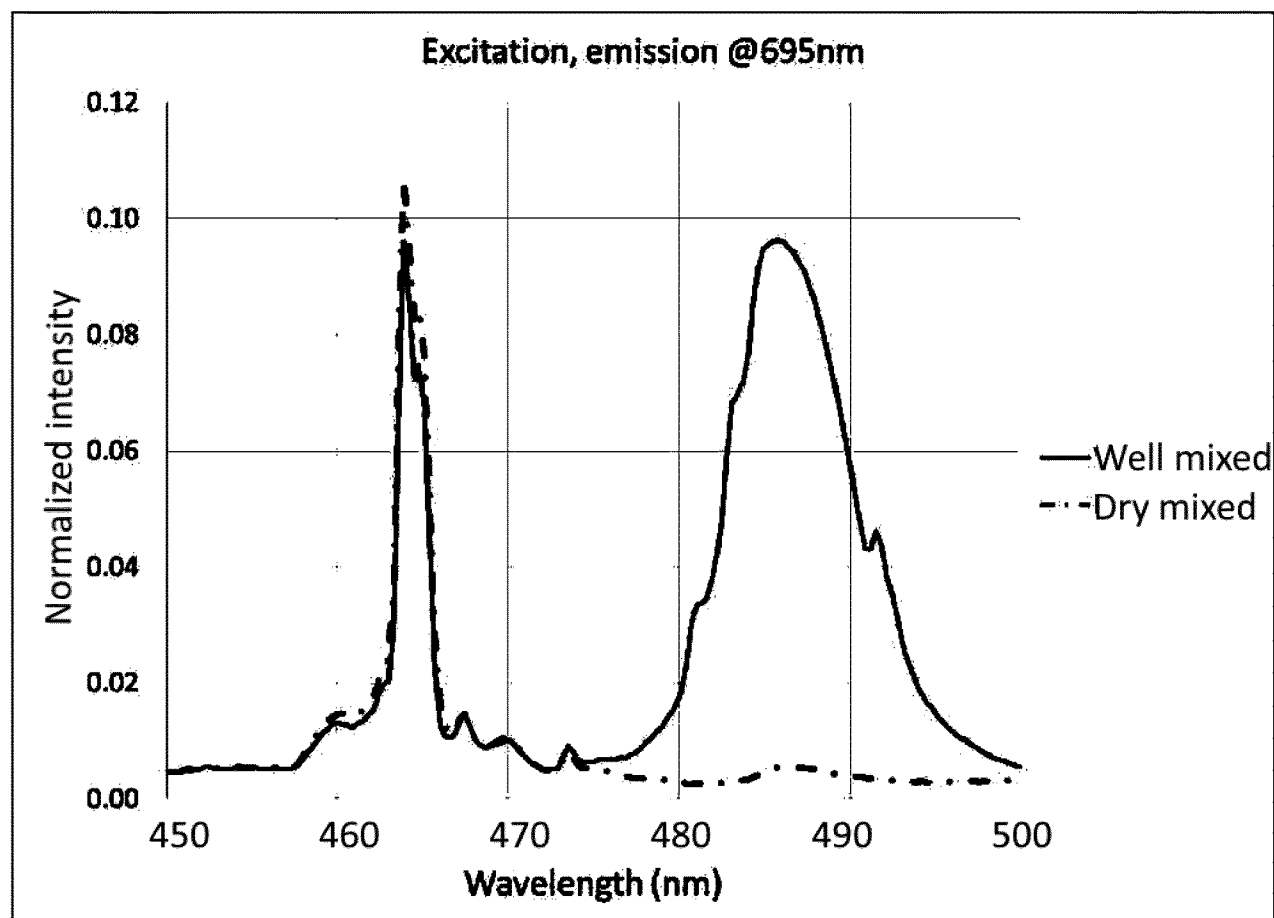


FIGURE 3

FIGURE 4



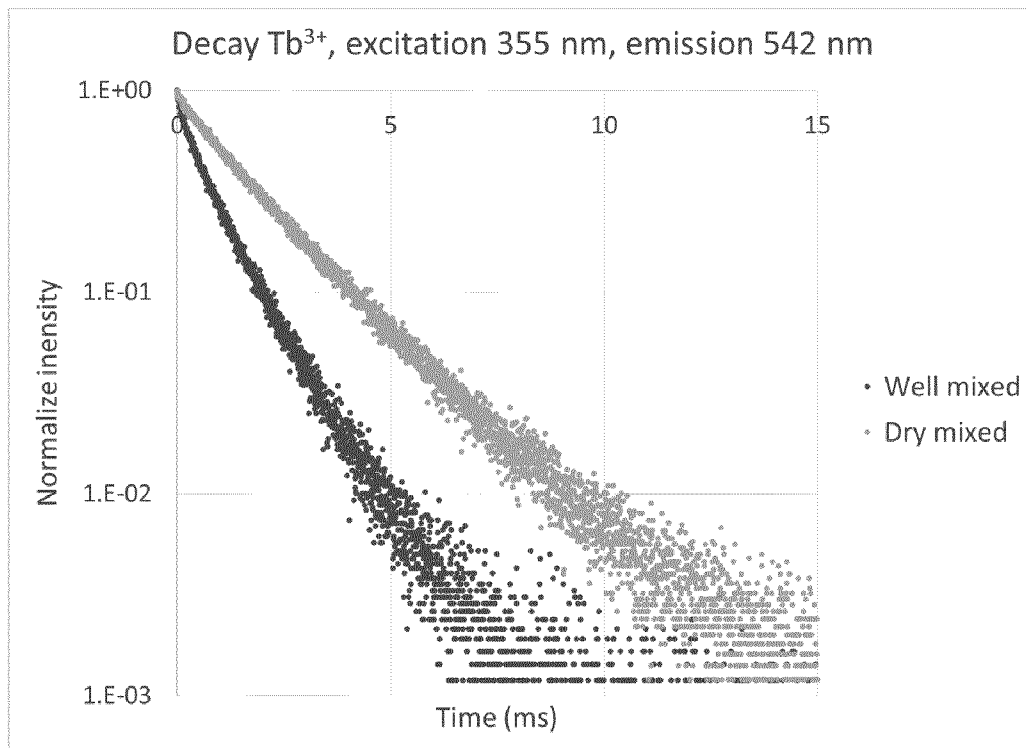


FIGURE 5

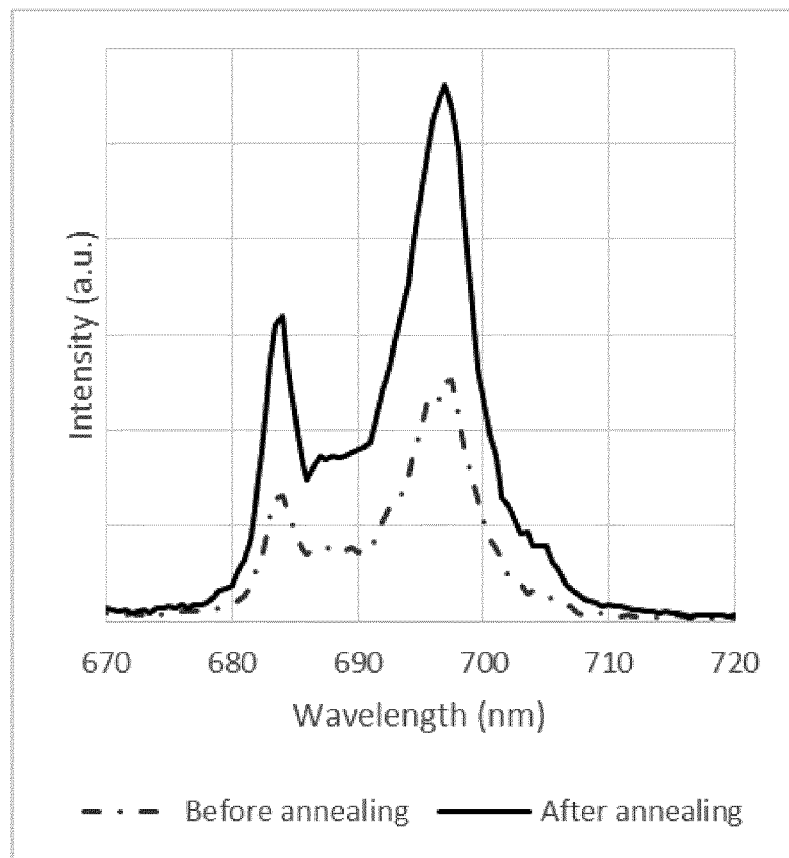


FIGURE 6

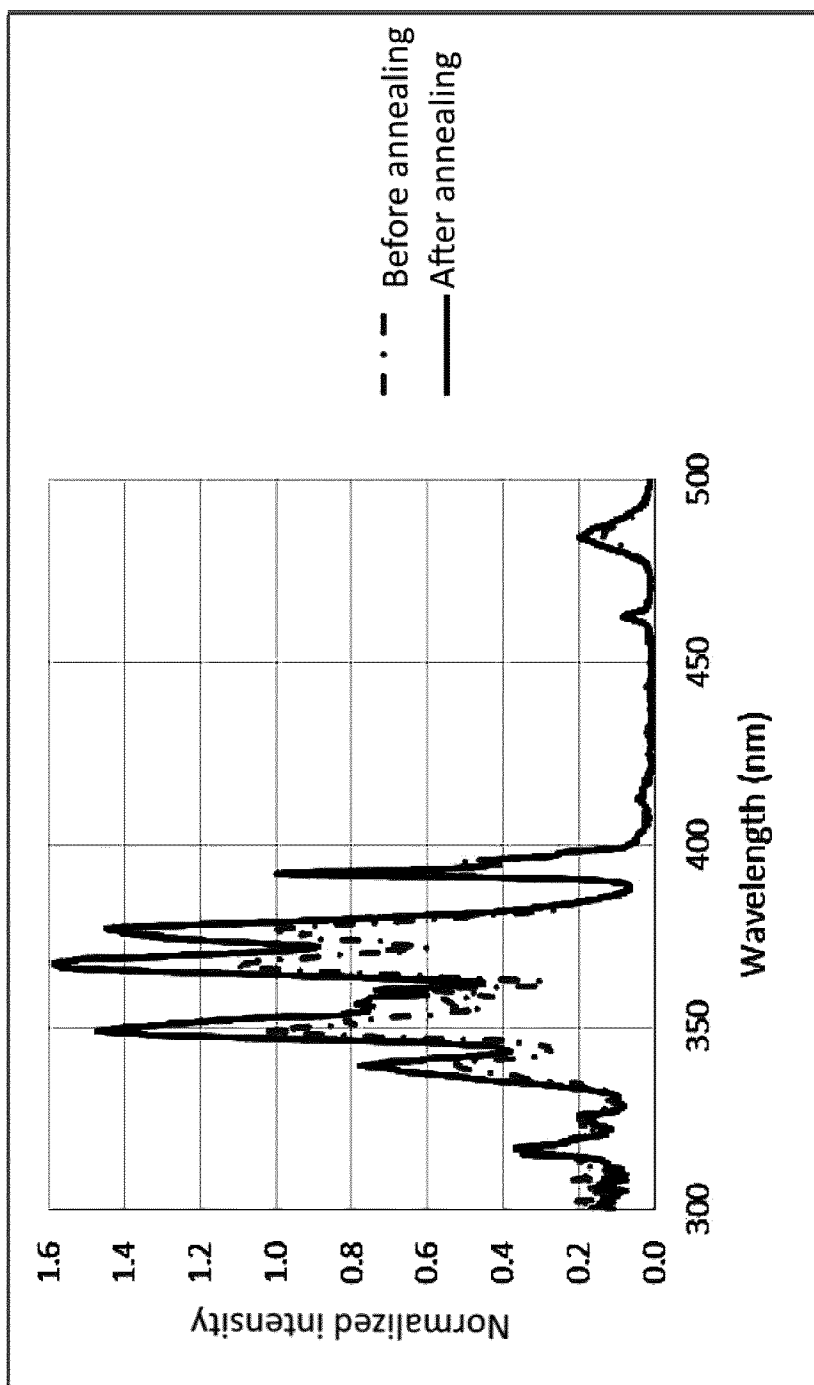


FIGURE 7

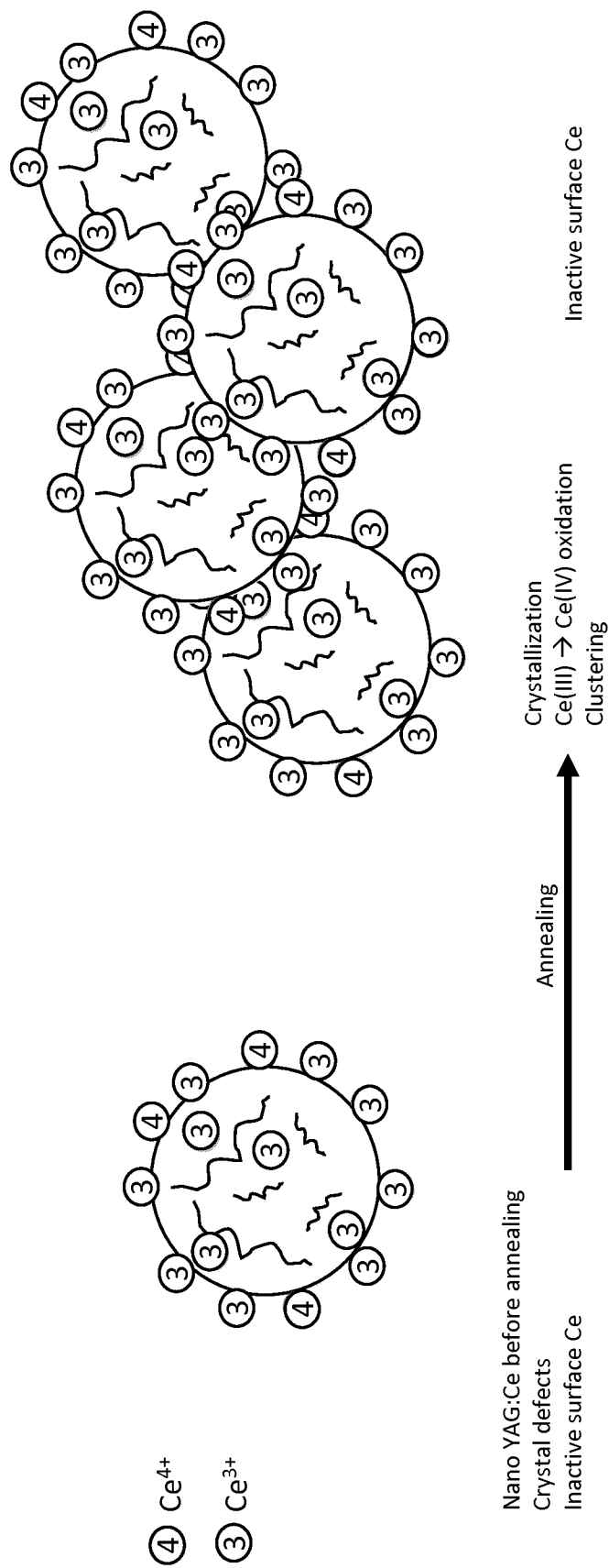


FIGURE 8

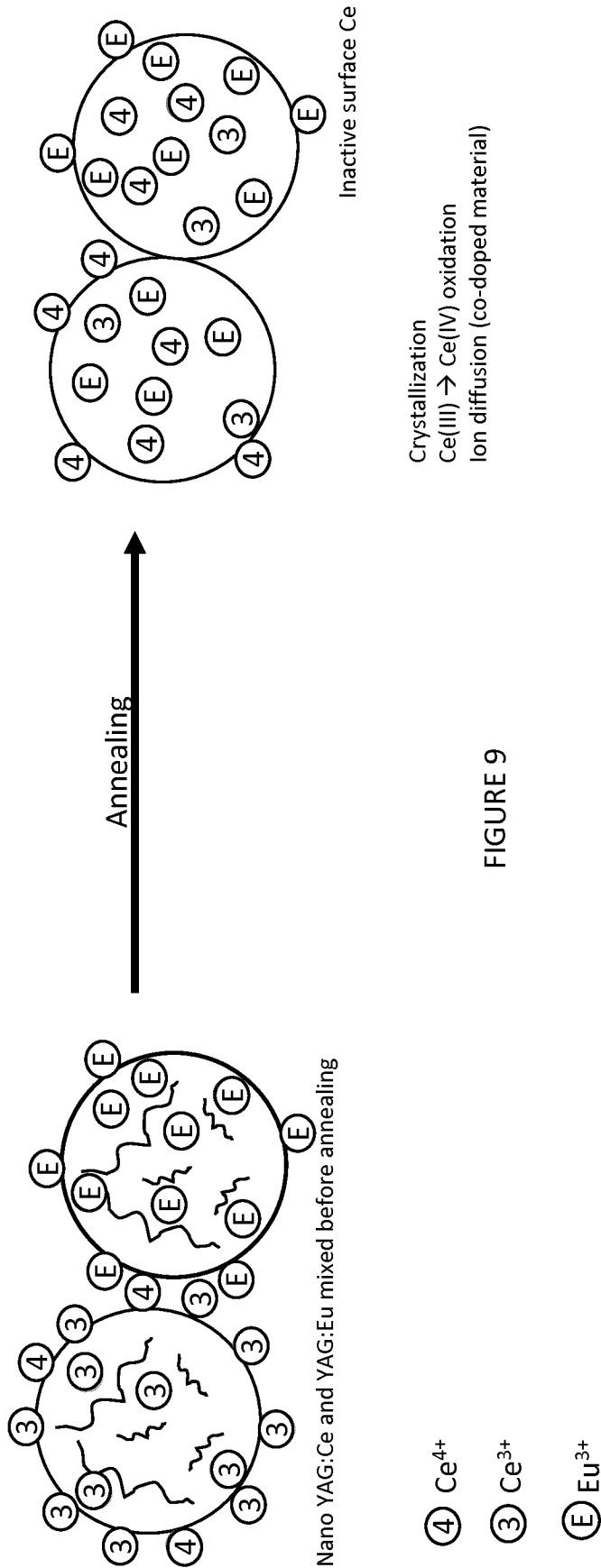


FIGURE 9

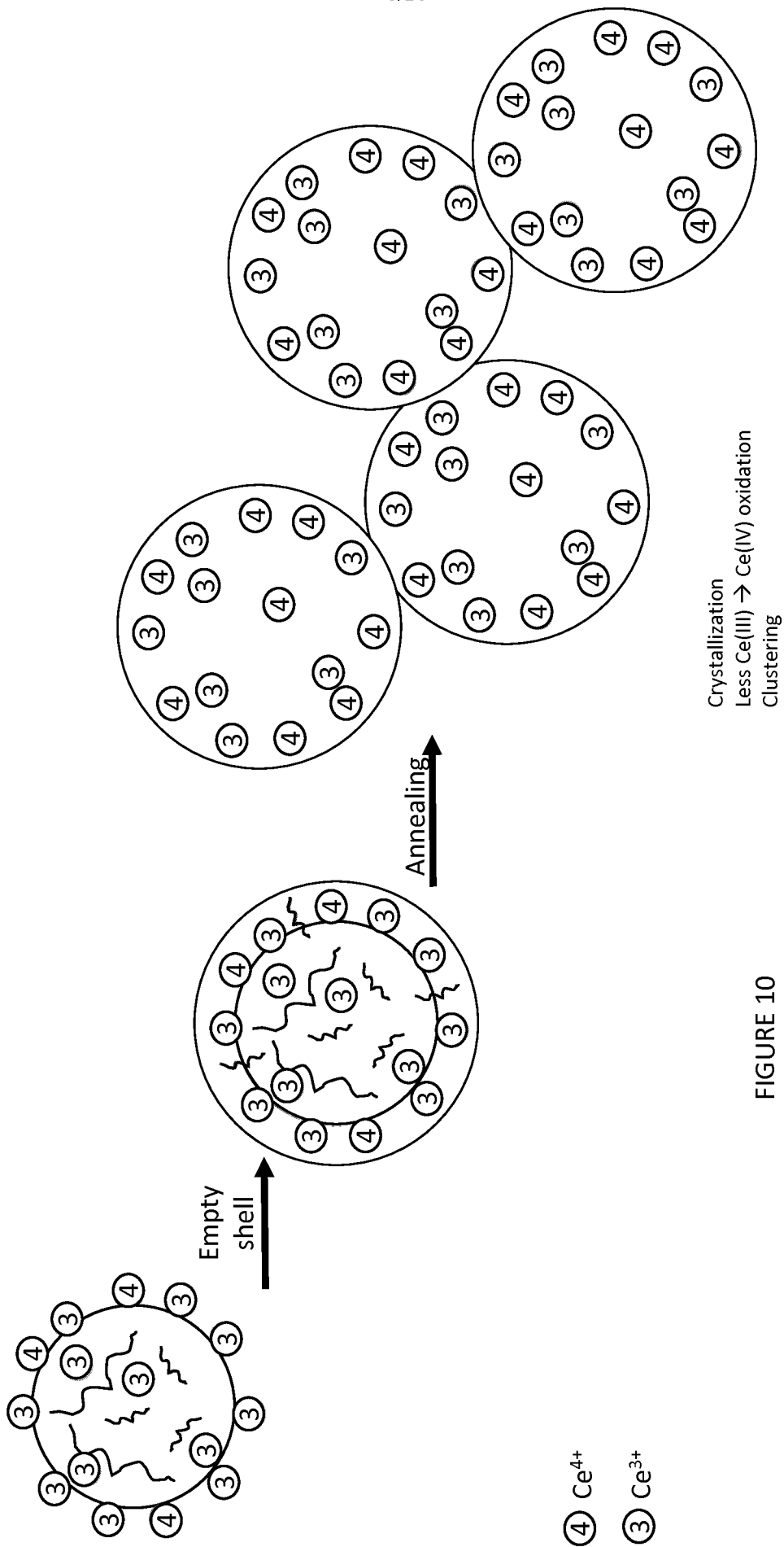


FIGURE 10

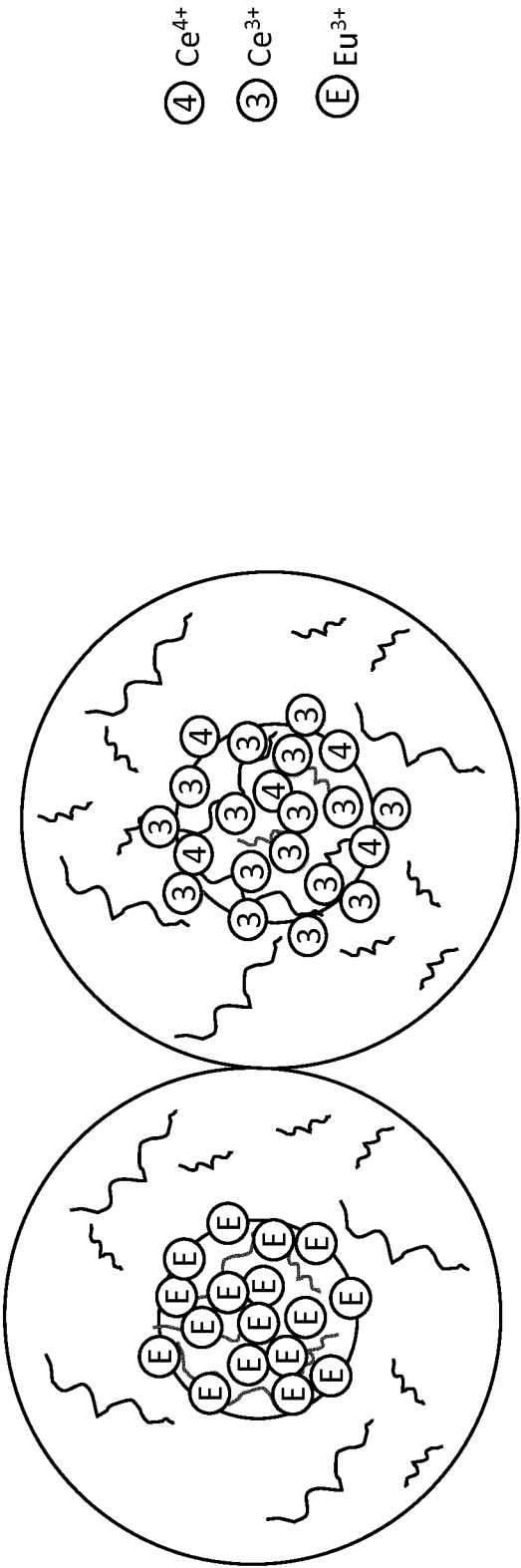


FIGURE 11

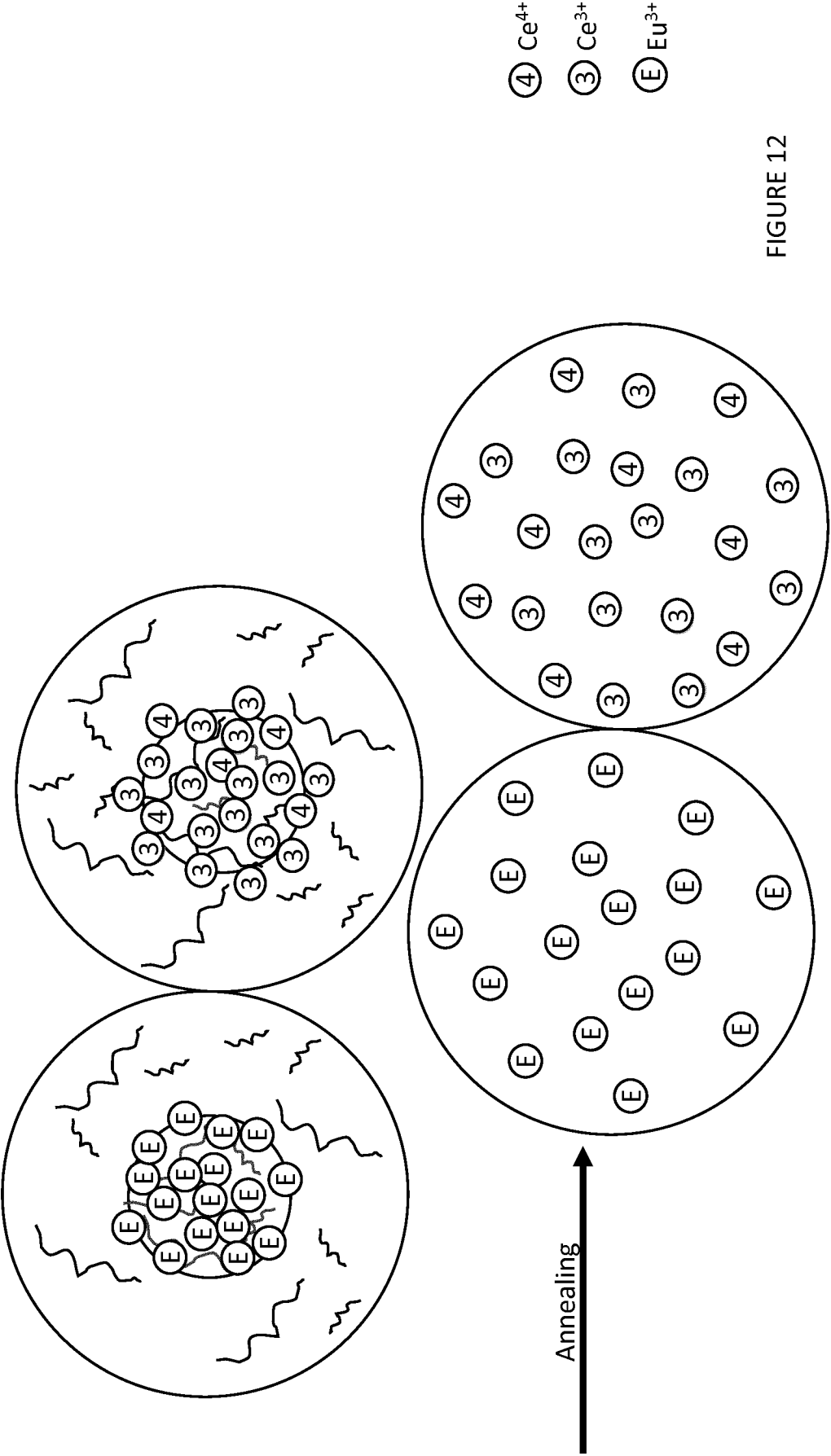


FIGURE 12

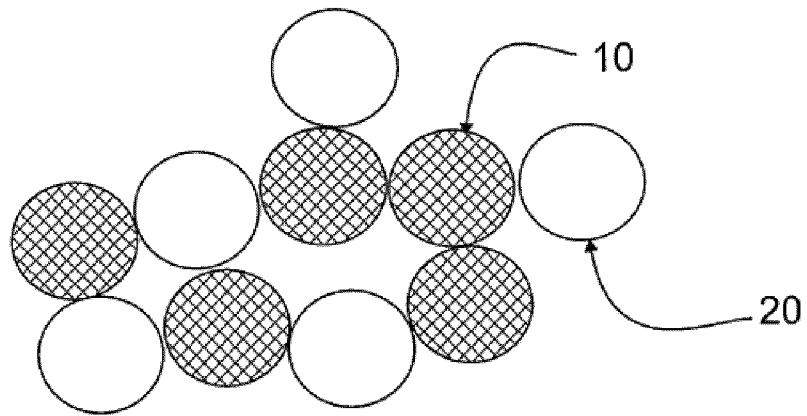


FIGURE 13

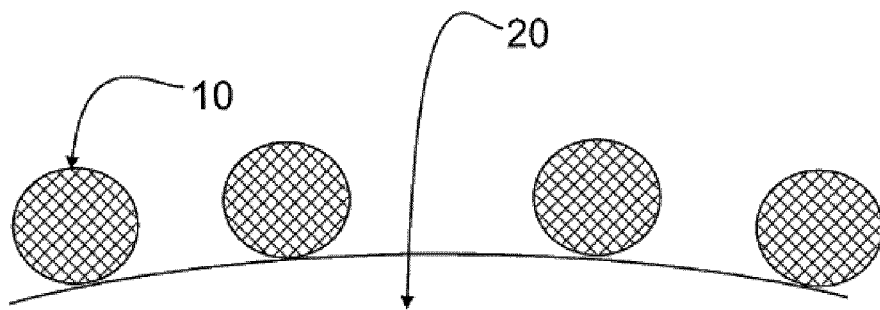


FIGURE 14

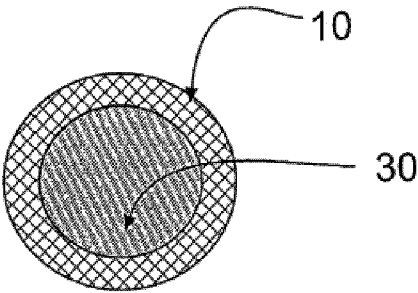


FIGURE 15

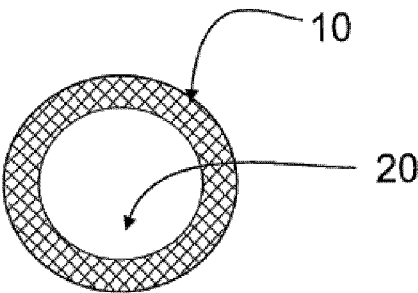


FIGURE 16

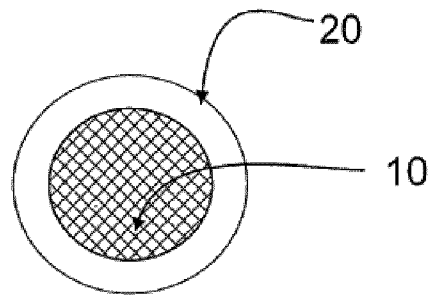


FIGURE 17

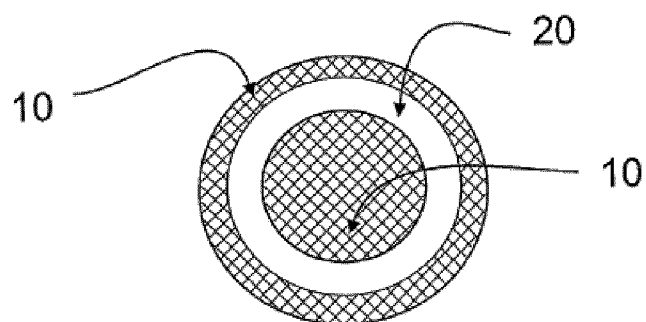


FIGURE 18

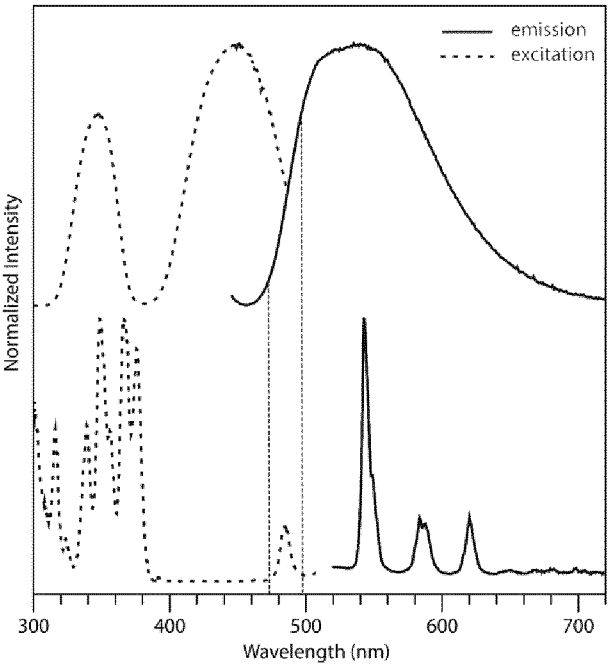


FIGURE 19

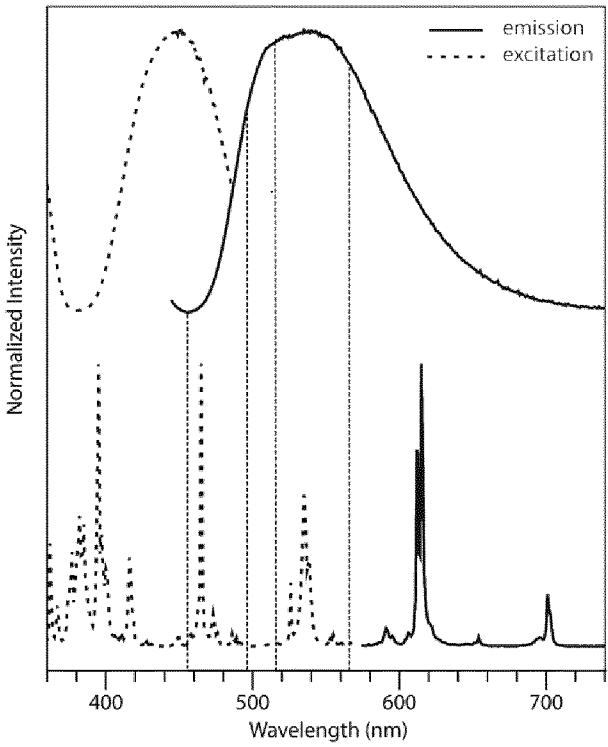


FIGURE 20