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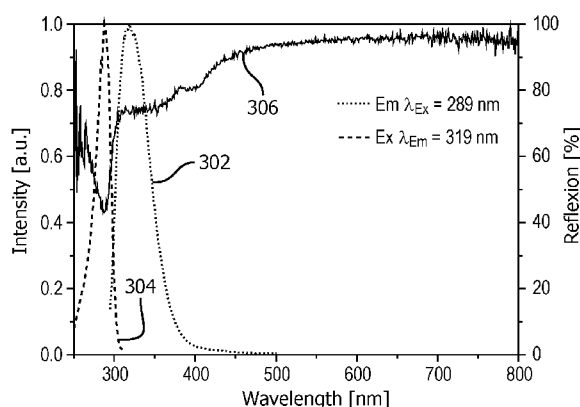
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(54) **Title:** Ce^{3+} ACTIVATED LUMINESCENT COMPOSITIONS FOR APPLICATION IN IMAGING SYSTEMS

**FIG. 3**

(57) **Abstract:** This disclosure relates to luminescent compositions comprising a host matrix sensitized by Ce^{3+} and showing emission in the ultraviolet range. Typical host matrices include fluorides, sulphates, and phosphates, in particular $\text{A}(\text{Y}_{1-x-y}\text{Lu}_x\text{La}_y)\text{F}_4$, $\text{A}(\text{Y}_{1-x-y}\text{Lu}_x\text{La}_y)_3\text{F}_{10}$, $\text{BaCa}(\text{Y}_{1-x-y}\text{Lu}_x\text{La}_y)_2\text{F}_{10}$, and $\text{Ba}(\text{Y}_{1-x-y}\text{Lu}_x\text{La}_y)_2\text{F}_8$, wherein $\text{A} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{or Cs}$. One or more of these luminescent compositions may be applied as a ceramic or single crystalline converter for CT, PET or SPECT scanners, or as a luminescent powder layer for x-ray intensifying screens.

Ce³⁺ ACTIVATED LUMINESCENT COMPOSITIONS FOR APPLICATION IN IMAGING SYSTEMS

The present application relates generally to the imaging arts and more particularly to luminescent compositions for use in imaging systems. The application subject matter finds
5 use in many kinds of imaging systems, including for example computed tomography (CT) imaging systems, positron emission tomography (PET) imaging systems, and single-photon emission computed tomography (SPECT) systems. It could also be used in connection with other imaging systems, for example as part of an x-ray intensifying screen.

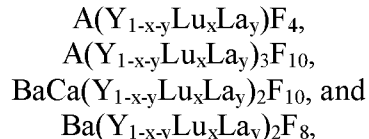
Luminescent compositions function to harness the energy of incoming high energy
10 radiation photons (e.g. x-rays or gamma rays) and transform that energy to secondary radiation photons (e.g. ultraviolet light) which can more easily be measured by electronic photodetectors such as a photodiode or photomultiplier. Each such transformation is called a scintillation event. The photodetector produces electrical signals indicative of the intensity of the secondary radiation. In a typical application, an imaging detector array includes several
15 pixels, with each pixel formed by one or more blocks of a scintillating luminescent composition material optically coupled to a photodetector.

The performance of a scintillating luminescent composition material depends on many properties of the material, including for example its stopping power, brightness, and decay time. Ever since the discovery of x-rays by Wilhelm Conrad Roentgen in 1895 there
20 has been an ongoing need to find and develop materials which are efficient in converting higher energy photons into lower energy photons. A wide variety of such scintillating materials have been investigated and used. Commonly used scintillating luminescent compositions for x-ray detection include for example Ce³⁺ doped inorganic host matrices such as Lu₂SiO₅, LuPO₄, and Lu₂Si₂O₇, all of which have a high density which provides an
25 advantageously high stopping power with respect to the incoming x-ray radiation.

Nonetheless, novel luminescent compositions are still of high interest, especially if their density or light yield is high, or if their rise and decay times are short. Regarding decay times in particular, a luminescent composition's decay time corresponds to the time it takes for the secondary scintillation light afterglow to fall back down to practically zero or to some
30 other minimum value. Generally speaking, it is desirable to reduce a luminescent

composition's decay time. Shorter decay times lead to a shorter imaging time, as well as a higher resolution in the imaging data. Similarly, an afterglow having a narrower wavelength spectrum is preferred to an afterglow having a broader wavelength spectrum. A smaller afterglow is advantageous because it increases the number of scintillation events which may be detected in a given time period, and also increases the temporal resolution of the detector. For these and other reasons the decay time is an essential performance figure of a respective luminescent composition, and shortening of the decay time yields advantages for the application.

The present disclosure relates to luminescent compositions sensitized by Ce^{3+} , and in particular to such luminescent compositions in which Ce^{3+} shows emission in the ultraviolet range. "Ultraviolet" light as defined herein corresponds to light having a wavelength between about 280 nm and about 400 nm. These luminescent compositions include for example scintillating compositions in which Ce^{3+} is located on crystallographic sites exerting a low crystal-field splitting and a low covalent interaction with the activator. Typical examples are fluorides, sulphates, and phosphates, in particular the following fluorides:



wherein A = Li, Na, K, Rb, Cs, or solid solution combinations thereof. The present disclosure also concerns the application of one or several of these luminescent compositions as a ceramic or single crystalline converter for CT imaging scanners, or PET or SPECT imaging scanners. This disclosure further concerns the application of one or several of these luminescent compositions in a luminescent powder layer for x-ray intensifying screens.

Numerous additional advantages and benefits will become apparent to those of ordinary skill in the art upon reading the following detailed description of the preferred embodiments. The invention may take form in various chemical compositions, various components and arrangements of components, and in various process operations and arrangements of process operations. The drawings are only for the purpose of illustrating preferred embodiments and are not to be construed as limiting the invention.

FIGURE 1 is a schematic cross-sectional view of an x-ray detector unit 100, not drawn to scale;

FIGURE 2 shows the x-ray diffraction pattern of $\text{KYF}_4:\text{Ce}$ ($\rho = 3.53 \text{ g/cm}^3$), versus an un-doped KYF_4 reference;

5 FIGURE 3 shows the emission 302, excitation 304, and reflection 306 spectra of $\text{KYF}_4:\text{Ce}$;

FIGURE 4 shows the decay curve of $\text{KYF}_4:\text{Ce}$ under 265 nm excitation (4f-5d) monitored at 327 nm;

10 FIGURE 5 shows the x-ray diffraction pattern of $\text{KY}_3\text{F}_{10}:\text{Ce}$ ($\rho = 4.27 \text{ g/cm}^3$), versus an un-doped KY_3F_{10} reference;

FIGURE 6 shows the emission 602, excitation 604, and reflection 606 spectra of $\text{KY}_3\text{F}_{10}:\text{Ce}$;

FIGURE 7 shows the decay curve of $\text{KY}_3\text{F}_{10}:\text{Ce}$ under 265 nm excitation (4f-5d) monitored at 377 nm;

15 FIGURE 8 shows the x-ray diffraction pattern of $\text{KLaF}_4:\text{Ce}$ ($\rho = 4.46 \text{ g/cm}^3$), versus an un-doped KLaF_4 reference;

FIGURE 9 shows the emission 902, excitation 904, and reflection 906 spectra of $\text{KLaF}_4:\text{Ce}$;

20 FIGURE 10 shows the decay curve of $\text{KLaF}_4:\text{Ce}$ under 265 nm excitation (4f-5d) monitored at 317 nm;

FIGURE 11 shows the x-ray diffraction pattern of $\text{KLuF}_4:\text{Ce}$ ($\rho = 4.80 \text{ g/cm}^3$), versus an un-doped KLuF_4 reference;

FIGURE 12 shows the emission 202, excitation 204, and reflection 206 spectra of $\text{KLuF}_4:\text{Ce}$;

25 FIGURE 13 shows the decay curve of $\text{KLuF}_4:\text{Ce}$ under 265 nm excitation (4f-5d) monitored at 312 nm;

FIGURE 14 shows the x-ray diffraction pattern of $\text{NaYF}_4:\text{Ce}$ ($\rho = 4.30 \text{ g/cm}^3$), versus an un-doped NaYF_4 reference;

30 FIGURE 15 shows the emission 502, excitation 504, and reflection 506 spectra of $\text{NaYF}_4:\text{Ce}$;

FIGURE 16 shows the decay curve of NaYF₄:Ce under 265 nm excitation (4f-5d) monitored at 295 nm;

FIGURE 17 shows the x-ray diffraction pattern of NaLuF₄:Ce ($\rho = 5.70 \text{ g/cm}^3$), versus an un-doped NaYF₄ reference;

5 FIGURE 18 shows two emission spectra 802a and 802b, the excitation spectrum 804, and the reflection 806 spectrum of NaLuF₄:Ce;

FIGURE 19 shows the decay curve of NaLuF₄:Ce under 265 nm excitation (4f-5d) monitored at 320 nm;

10 FIGURE 20 shows the x-ray diffraction pattern of RbLaF₄:Ce ($\rho = 4.94 \text{ g/cm}^3$), versus an un-doped RbLaF₄ reference;

FIGURE 21 shows the emission 102, excitation 104, and reflection 106 spectra of RbLaF₄:Ce; and

FIGURE 22 shows the decay curve of RbLaF₄:Ce under 265 nm excitation (4f-5d) monitored at 310 nm.

15 FIGURE 1 illustrates a first, exemplary embodiment of a unit 100 which detects incoming high energy radiation 50. The radiation detector unit 100 may be used, for example, in a computed tomography (CT) imaging apparatus. CT is an imaging modality used in many different contexts, including medical imaging. CT imaging systems typically employ an x-ray source (not shown) to generate x-rays 50 that traverse an examination region. A subject
20 arranged in the examination region interacts with and absorbs a portion of the traversing x-rays 50. An array of x-ray radiation detectors 100 is arranged opposite the x-ray source to detect and measure intensities of the transmitted x-rays 50. The radiation detector array typically includes several detectors 100, wherein each detector 100 corresponds to one imaging pixel.

25 In an alternative example, the radiation detector unit 100 may be used in a positron emission tomography (PET) imaging apparatus. PET is an imaging modality used in many different contexts, including medical imaging. In PET, the subject to be imaged typically ingests a radiopharmaceutical which is configured to travel to an area of the subject to be imaged. The radiopharmaceutical emits gamma rays 50 which travel through and out of the
30 subject to be detected by an array of gamma ray radiation detectors 100 arranged around the

subject to detect and measure intensities of the emitted gamma rays 50. The radiation detector array typically includes several detectors 100, wherein each detector 100 corresponds to one imaging pixel.

Regardless of the particular imaging apparatus, the radiation detector 100 operates in substantially the same manner. The radiation detector 100 interacts with the incoming radiation 50 to produce electronic signals representative of the intensity and spectrum of radiation 50 received by the detector 100. The electronic signals may then be electronically processed to produce a two-dimensional or three-dimensional image of the subject under investigation. FIGURE 1 is schematic in nature, meant principally for illustration and not as an exact depiction to scale of the elements shown. Therefore, the dimensions of a given element in relation to the dimensions of other elements as shown in the Figure do not necessarily reflect such relative dimensions as one would find in an actual radiation detector unit. For example, in an actual radiation detector unit, the reflector material 22 would be much thinner in relation to the size of the scintillator 10 than illustrated in the Figure.

The radiation detector unit 100 includes a scintillating luminescent composition 10 which, from the perspective of the view in FIGURE 1, has a top face 12, a bottom face 14, and four side faces. Only two side faces 16 and 18 are shown in the Figure. The relative terms “top”, “bottom” and “side” have meaning only from the perspective of FIGURE 1. They do not have any functional significance in the operation of the detector 100. Thus, in particular applications, the detector 100 may be placed in an imaging apparatus such that the face 12 is actually a bottom face.

The x-ray detector unit 100 functions to harness the incoming high energy radiation 50 impinging upon the top face 12 and produce an electric signal which is representative of the amount or total energy of detected radiation 50. The first step in this process is performed by the scintillator 10, which acts as a transducer by absorbing the energy of the incoming high energy radiation 50 and converting that energy to secondary photons 52. The amount of secondary photons 52 produced by the scintillator 10 is thus representative of the incoming radiation energy absorbed within a given reading time period. Many different scintillators 10 are known in the art, and various scintillator 10 embodiments are discussed further below.

The demands of a particular application may render one or more scintillator(s) 10 particularly suitable or particularly unsuitable for that application.

The x-ray detector unit 100 includes a photodetector 20 optically coupled to the bottom face 14 of the scintillator 10. Such optical coupling may be achieved by a direct
5 contact, or with intervening elements such as for example filters, transparent or semi-transparent layers, transparent or semi-transparent adhesive, light guides, and the like. The photodetector 20 absorbs the energy of the secondary photons 52 produced by the scintillator 10 and converts that energy to an electrical signal. The electrical signal produced by the photodetector 20 is representative of the amount of secondary photons 52 impinging upon the
10 photodetector 20, and is thus also representative of the radiation 50 flux entering the detector 100. Photodetectors include photomultipliers, photodiodes, and the like.

The scintillator 10 is covered with a reflector material 22 on each portion of its exterior other than the region where the scintillator 10 is optically coupled to the photodetector 20. The reflector material 22 reflects the secondary photons 52, but permits the high energy
15 radiation photons 50 to pass through unaffected. Thus, the secondary photons 52 must exit the scintillator 10 (if they exit at all) through the photodetector 20 (except some small loss). Some secondary photons 52 will be self-absorbed by the scintillator 10 before they can reach the photodetector 20, and some may escape through or around the reflector material 22.

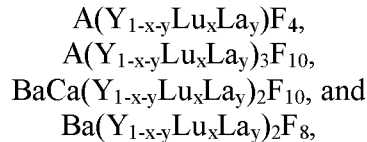
To help ensure that each radiation detector unit 100 counts only the radiation 50
20 which impinges upon the top face 12 of that unit 100, a radiation shielding or reflecting material 28 is placed in the spaces between the top faces 12 of adjacent units 100. For example, common x-ray shielding materials 28 include lead and tungsten, both of which substantially prevent the passage of any x-rays through the shield 28.

The photodetector 20 has one or more electrical leads 30 connecting the
25 photodetector 20 to a circuit board 32. The circuit board 32 receives electrical signals from the photodetector 20 and passes them on to signal processing hardware and further on to an image processor 34. The image processor 34 processes electrical signals received from several different radiation detector units 100 to form an image of the subject under investigation according to a mathematical algorithm or algorithms. The image can be displayed on an
30 associated display 36. A user input 38 may be provided for a user to control the image

processor 34. The image processor 34 may store related imaging data and other data in a memory 40.

In yet another example, the luminescent compositions of the present disclosure may be used as an x-ray intensifier screen (not shown). In such embodiments, the luminescent composition is typically in a powdered form, rather than the ceramic or single crystal form of the scintillator 10 shown in FIGURE 1.

The present disclosure particularly pertains to a luminescent composition scintillator having a host matrix which incorporates Ce^{3+} as an activator. In some embodiments, for example, the Ce^{3+} may comprise from 0.01% to 10% by atomic number within the host matrix. The Ce^{3+} dopant shows luminescence in the ultraviolet range due to its spin- and parity-allowed $[\text{Xe}]5d^1 - [\text{Xe}]4f^1$ transition. The luminescent compositions of the present disclosure may include one or more other doping agents in addition to the Ce^{3+} . These co-activators may include, for example, Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} , or Yb^{3+} . Typical examples of a suitable host lattice include fluorides, sulphates, and phosphates, in particular:



wherein $\text{A} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$, or solid solutions thereof. Also, $0 \leq x \leq 1$ and $0 \leq y \leq 1$, with $x+y \leq 1$.

The present disclosure also concerns the application of one or several of these luminescent compositions as a ceramic or single crystalline converter for CT imaging scanners, or PET or SPECT imaging scanners. This disclosure further concerns the application of one or several of these luminescent compositions in a luminescent powder layer for x-ray intensifying screens. The following table gives an overview of some representative example luminescent compositions:

Table 1:
Density, Peak Emission, and Decay Time of Luminescent Compositions.

Example No.	Chemical Composition	Density [g/cm ³]	Emission maximum [nm]	Decay time 1/e [ns]
1	KYF ₄ :Ce	3.53	327	31
2	KY ₃ F ₁₀ :Ce	4.27	377	45
3	KLaF ₄ :Ce	4.46	317	26
4	KLuF ₄ :Ce	4.80	312	29
5	NaYF ₄ :Ce	4.30	295	23
6	NaLuF ₄ :Ce	5.70	310	33
7	RbLaF ₄ :Ce	4.94	310	26
8	BaYF ₅ :Ce	5.25	330	41
9	NaLaF ₄ :Ce	4.66		
10	KLu ₃ F ₁₀ :Ce	6.78		
11	CsLaF ₄ :Ce			
12	BaY ₂ F ₈ :Ce	5.02		
13	Ba ₄ Y ₃ F ₁₇ :Ce	5.24		
14	BaLu ₂ F ₈ :Ce	6.98		
15	BaCaLu ₂ F ₁₀ :Ce	6.54		

Such materials can result in one or more of several advantages. These advantages can include lower production costs due to less material being required, a higher imaging resolution, and a shorter imaging time.

The luminescent compositions of the present disclosure may further include a diffusion barrier which coats the particles, the ceramic, or the single crystal of the composition. The diffusion barrier material operates to substantially prevent diffusion of H₂O, CO₂ and volatile organic compounds across the diffusion barrier. This enhances the stability of the luminescent composition.

The luminescent compositions of the present disclosure can be produced and used in the same manner as conventional luminescent compositions, as known by one of ordinary skill in the art.

The following working examples are provided to more thoroughly describe the luminescent compositions of the present disclosure.

EXAMPLE 1

KYF₄:Ce(1%) was prepared and evaluated. Initially, the first three ingredients of the following table were thoroughly blended together in an agate mortar:

Ingredient	Amount
KF	0.852 g (14.7 mmol)
YF ₃	2.119 g (14.5 mmol)
CeF ₃	0.029 g (0.18 mmol)
KBF ₄	0.030 g (1 wt-%)

KBF₄ was then added to the initial three ingredient blend, in the amount identified in the table, and the resulting mixture was milled again to form a final blend. The final blend was filled into a glassy-carbon crucible and calcined at 650° C for 6 hours. A small sample of AlF₃ was used as a water scavenger in the tube furnace to trap any water remaining in the stream of dried Nitrogen. After the firing step, samples were powderized by grinding in an agate mortar.

FIGURE 2 shows the x-ray diffraction pattern of the resulting KYF₄:Ce ($\rho = 3.53 \text{ g/cm}^3$), versus an un-doped KYF₄ reference.

FIGURE 3 shows the emission 302, excitation 304, and reflection 306 spectra of the resulting KYF₄:Ce.

FIGURE 4 shows the decay curve of the resulting KYF₄:Ce under 265 nm excitation (4f-5d) monitored at 327 nm.

EXAMPLE 2

KY₃F₁₀:Ce(1%) was prepared and evaluated. Initially, the first three ingredients of the following table were thoroughly blended together in an agate mortar:

Ingredient	Amount
KF	0.350 g (6.0 mmol)
YF ₃	2.614 g (17.9 mmol)
CeF ₃	0.036 g (0.23 mmol)
KBF ₄	0.030 g (1 wt-%)

KBF₄ was then added to the initial three ingredient blend, in the amount identified in the table, and the resulting mixture was milled again to form a final blend. The final blend was filled into a glassy-carbon crucible and calcined at 650° C for 6 hours. A small sample of AlF₃ was used as a water scavenger in the tube furnace to trap any water remaining in the stream of dried Nitrogen. After the firing step, samples were powderized by grinding in an agate mortar.

FIGURE 5 shows the x-ray diffraction pattern of the resulting KY₃F₁₀:Ce ($\rho = 4.27 \text{ g/cm}^3$), versus an un-doped KY₃F₁₀ reference.

FIGURE 6 shows the emission 602, excitation 604, and reflection 606 spectra of the resulting $\text{KY}_3\text{F}_{10}:\text{Ce}$. The band at 327 nm is due to an impurity of $\text{KYF}_4:\text{Ce}$.

FIGURE 7 shows the decay curve of the resulting $\text{KY}_3\text{F}_{10}:\text{Ce}$ under 265 nm excitation (4f-5d) monitored at 377 nm.

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EXAMPLE 3

$\text{KLaF}_4:\text{Ce}(1\%)$ was prepared and evaluated. Initially, the first three ingredients of the following table were thoroughly blended together in an agate mortar:

Ingredient	Amount
KF	0.686 g (11.8 mmol)
LaF_3	2.291 g (11.7 mmol)
CeF_3	0.029 g (0.18 mmol)
KBF_4	0.030 g (1 wt-%)

KBF_4 was then added to the initial three ingredient blend, in the amount identified in the table, and the resulting mixture was milled again to form a final blend. The final blend was filled
10 into a glassy-carbon crucible and calcined at 650°C for 6 hours. A small sample of AlF_3 was used as a water scavenger in the tube furnace to trap any water remaining in the stream of dried Nitrogen. After the firing step, samples were powderized by grinding in an agate mortar.

FIGURE 8 shows the x-ray diffraction pattern of the resulting $\text{KLaF}_4:\text{Ce}$ ($\rho = 4.46\text{ g/cm}^3$), versus an un-doped KLaF_4 reference.

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FIGURE 9 shows the emission 902, excitation 904, and reflection 906 spectra of the resulting $\text{KLaF}_4:\text{Ce}$.

FIGURE 10 shows the decay curve of the resulting $\text{KLaF}_4:\text{Ce}$ under 265 nm excitation (4f-5d) monitored at 317 nm.

EXAMPLE 4

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$\text{KLuF}_4:\text{Ce}(1\%)$ was prepared and evaluated. Initially, the first three ingredients of the following table were thoroughly blended together in an agate mortar:

Ingredient	Amount
KF	0.602 g (10.4 mmol)
LuF_3	2.378 g (10.3 mmol)
CeF_3	0.020 g (0.13 mmol)
KBF_4	0.030 g (1 wt-%)

KBF₄ was then added to the initial three ingredient blend, in the amount identified in the table, and the resulting mixture was milled again to form a final blend. The final blend was filled into a glassy-carbon crucible and calcined at 650° C for 6 hours. A small sample of AlF₃ was used as a water scavenger in the tube furnace to trap any water remaining in the stream of dried Nitrogen. After the firing step, samples were powderized by grinding in an agate mortar.

FIGURE 11 shows the x-ray diffraction pattern of the resulting KLuF₄:Ce ($\rho = 4.80 \text{ g/cm}^3$), versus an un-doped KYF₄ reference. X-ray diffraction pattern data for un-doped KLuF₄ was not readily available to the inventors at the time this disclosure was prepared.

FIGURE 12 shows the emission 202, excitation 204, and reflection 206 spectra of the resulting KLuF₄:Ce.

FIGURE 13 shows the decay curve of the resulting KLuF₄:Ce under 265 nm excitation (4f-5d) monitored at 312 nm.

EXAMPLE 5

NaYF₄:Ce(1%) was prepared and evaluated. Initially, the first three ingredients of the following table were thoroughly blended together in an agate mortar:

Ingredient	Amount
NaF	0.669 g (15.9 mmol)
YF ₃	2.300 g (15.8 mmol)
CeF ₃	0.031 g (0.19 mmol)
NaBF ₄	0.030 g (1 wt-%)

NaBF₄ was then added to the initial three ingredient blend, in the amount identified in the table, and the resulting mixture was milled again to form a final blend. The final blend was filled into a glassy-carbon crucible and calcined at 700° C for 6 hours. A small sample of AlF₃ was used as a water scavenger in the tube furnace to trap any water remaining in the stream of dried Nitrogen. After the firing step, samples were powderized by grinding in an agate mortar.

FIGURE 14 shows the x-ray diffraction pattern of the resulting NaYF₄:Ce ($\rho = 4.30 \text{ g/cm}^3$), versus an un-doped NaYF₄ reference.

FIGURE 15 shows the emission 502, excitation 504, and reflection 506 spectra of the resulting NaYF₄:Ce.

FIGURE 16 shows the decay curve of the resulting NaYF₄:Ce under 265 nm excitation (4f-5d) monitored at 295 nm.

EXAMPLE 6

NaLuF₄:Ce(1%) was prepared and evaluated. Initially, the first three ingredients of the following table were thoroughly blended together in an agate mortar:

Ingredient	Amount
NaF	0.460 g (11.0 mmol)
LuF ₃	2.518 g (10.9 mmol)
CeF ₃	0.022 g (0.14 mmol)
NaBF ₄	0.030 g (1 wt-%)

NaBF₄ was then added to the initial three ingredient blend, in the amount identified in the table, and the resulting mixture was milled again to form a final blend. The final blend was filled into a glassy-carbon crucible and calcined at 700° C for 6 hours. A small sample of AlF₃ was used as a water scavenger in the tube furnace to trap any water remaining in the stream of dried Nitrogen. After the firing step, samples were powderized by grinding in an agate mortar.

FIGURE 17 shows the x-ray diffraction pattern of the resulting NaLuF₄:Ce ($\rho = 5.70 \text{ g/cm}^3$), versus an un-doped NaYF₄ reference. X-ray diffraction pattern data for un-doped NaLuF₄ was not readily available to the inventors at the time this disclosure was prepared.

FIGURE 18 shows a first emission spectrum 802a under 260 nm excitation light, a second emission spectrum 802b under 295 nm excitation light, the excitation spectrum 804, and the reflection spectrum 806 of the resulting NaLuF₄:Ce.

FIGURE 19 shows the decay curve of the resulting NaLuF₄:Ce under 265 nm excitation (4f-5d) monitored at 320 nm.

EXAMPLE 7

RbLaF₄:Ce(1%) was prepared and evaluated. Initially, the first three ingredients of the following table were thoroughly blended together in an agate mortar:

Ingredient	Amount
RbF	1.043 g (10.0 mmol)
LaF ₃	1.937 g (9.9 mmol)
CeF ₃	0.020 g (0.13 mmol)
RbBF ₄	0.030 g (1 wt-%)

RbBF₄ was then added to the initial three ingredient blend, in the amount identified in the table, and the resulting mixture was milled again to form a final blend. The final blend was filled into a glassy-carbon crucible and calcined at 700° C for 6 hours. A small sample of AlF₃ was used as a water scavenger in the tube furnace to trap any water remaining in the stream of dried Nitrogen. After the firing step, samples were powderized by grinding in an agate mortar.

FIGURE 20 shows the x-ray diffraction pattern of the resulting RbLaF₄:Ce ($\rho = 4.94 \text{ g/cm}^3$), versus an un-doped RbLaF₄ reference.

FIGURE 21 shows the emission 102, excitation 104, and reflection 106 spectra of the resulting RbLaF₄:Ce.

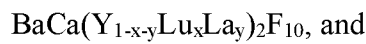
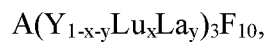
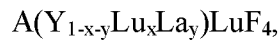
FIGURE 22 shows the decay curve of the resulting RbLaF₄:Ce under 265 nm excitation (4f-5d) monitored at 310 nm.

The invention has been described with reference to the preferred embodiments. Obviously, modifications and alterations will occur to others upon reading and understanding the preceding detailed description. It is intended that the invention be construed as including all such modifications and alterations insofar as they come within the scope of the appended claims or the equivalents thereof. The invention may take form in various chemical compositions, components and arrangements, combinations and sub-combinations of the elements of the disclosed embodiments.

CLAIMS

Having thus described the preferred embodiments, the invention is now claimed to be:

1. A scintillator material comprising a host lattice activated by Ce^{3+} , wherein the host lattice is selected from the group consisting of:

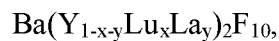
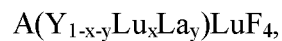


and further wherein A is selected from the group consisting of Li, Na, K, Rb, Cs, and a solid solution comprising a mixture of two or more of those elements, and

wherein $0 \leq x \leq 1$ and $0 \leq y \leq 1$.

2. The scintillator material of claim 1, wherein the material is activated by 0.01% to 10% of Ce^{3+} .
3. The scintillator material of claim 1, wherein the material is co-activated by at least one element selected from the group consisting of Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} , and Yb^{3+} .
4. The scintillator material of claim 1, further comprising a diffusion barrier coating material which substantially prevents diffusion of H_2O , CO_2 and volatile organic compounds across the diffusion barrier.
5. A PET or SPECT imaging system comprising the scintillator material of claim 1.
6. A CT imaging system comprising the scintillator material of claim 1.

7. An imaging system including an x-ray converter film which comprises the scintillator material of claim 1.
8. A luminescent composition comprising a host matrix in combination with Ce^{3+} as an activator, in which the emission band maximum of the Ce^{3+} is equal to or below 400 nm.
9. The luminescent composition of claim 8, wherein the emission band maximum of the Ce^{3+} is equal to or above 280 nm.
10. The luminescent composition of claim 8, wherein the host matrix is selected from the group consisting of:



and further wherein A is selected from the group consisting of Li, Na, K, Rb, Cs, and a solid solution comprising a mixture of two or more of those elements, and

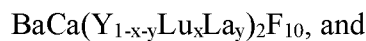
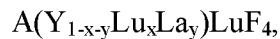
wherein $0 \leq x \leq 1$ and $0 \leq y \leq 1$.

11. The luminescent composition of claim 8, wherein the composition is activated by 0.01% to 10% of Ce^{3+} .
12. The luminescent composition of claim 8, wherein the composition is co-activated by at least one element selected from the group consisting of Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} , and Yb^{3+} .

13. The luminescent composition of claim 8, further comprising a diffusion barrier coating material which substantially prevents diffusion of H₂O, CO₂ and volatile organic compounds across the diffusion barrier.
14. An imaging system including an x-ray converter film which comprises the luminescent composition of claim 8.
15. A radiation detector including an x-ray converter film which comprises the luminescent composition of claim 8.
16. An imaging device comprising:

at least one radiation (50) source;

at least one radiation detector (100) including a scintillator material (10) comprising a rigid host lattice activated by Ce³⁺, wherein the host lattice is selected from the group consisting of:



and further wherein A is selected from the group consisting of Li, Na, K, Rb, Cs, and a solid solution comprising a mixture of two or more of those elements, and

wherein $0 \leq x \leq 1$ and $0 \leq y \leq 1$; and

a photodetector (20) optically coupled to the scintillator material (10).

17. The imaging device (100) of claim 16, wherein the imaging device (100) is a CT, PET, or SPECT imaging device.

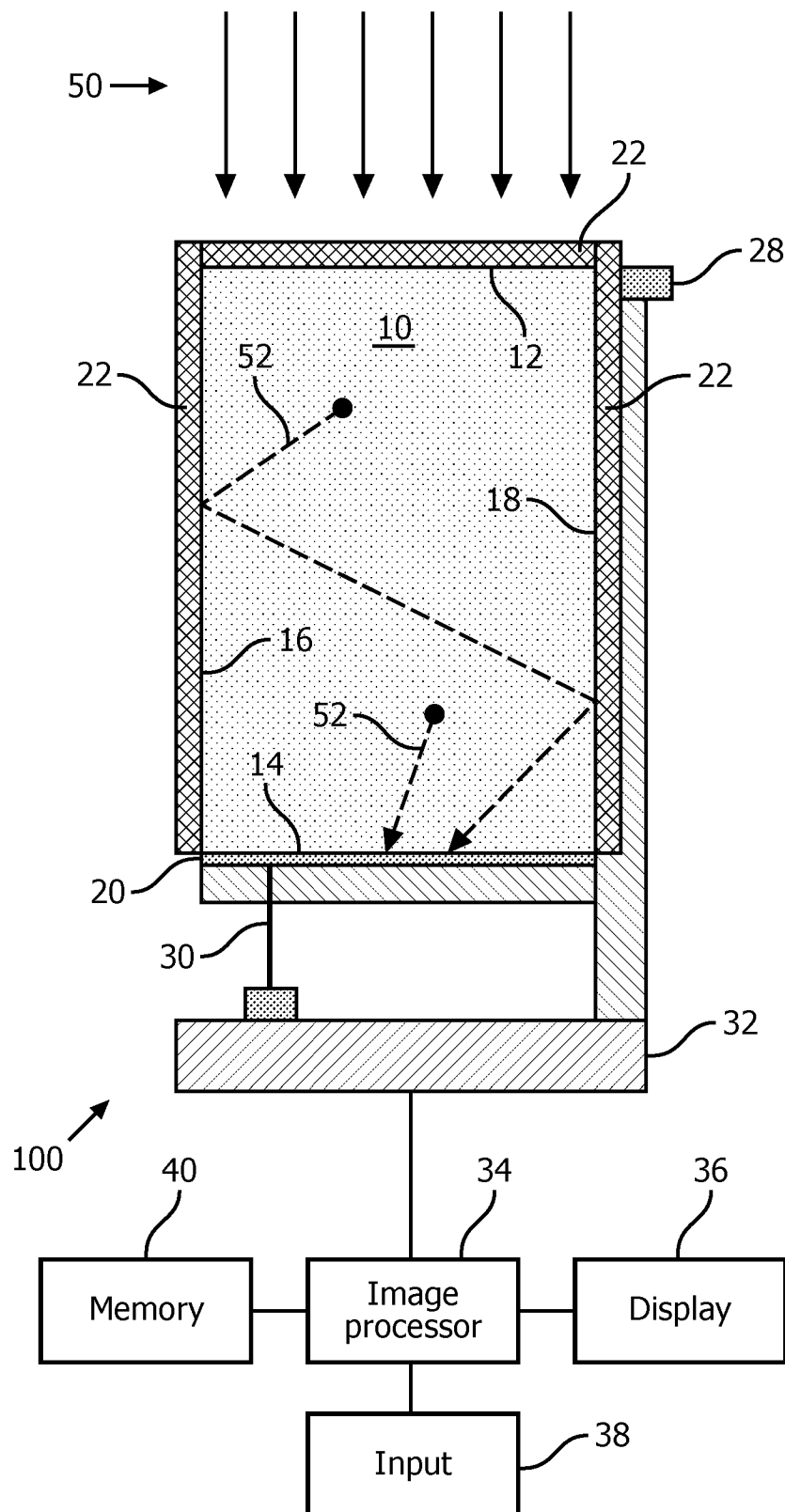


FIG. 1

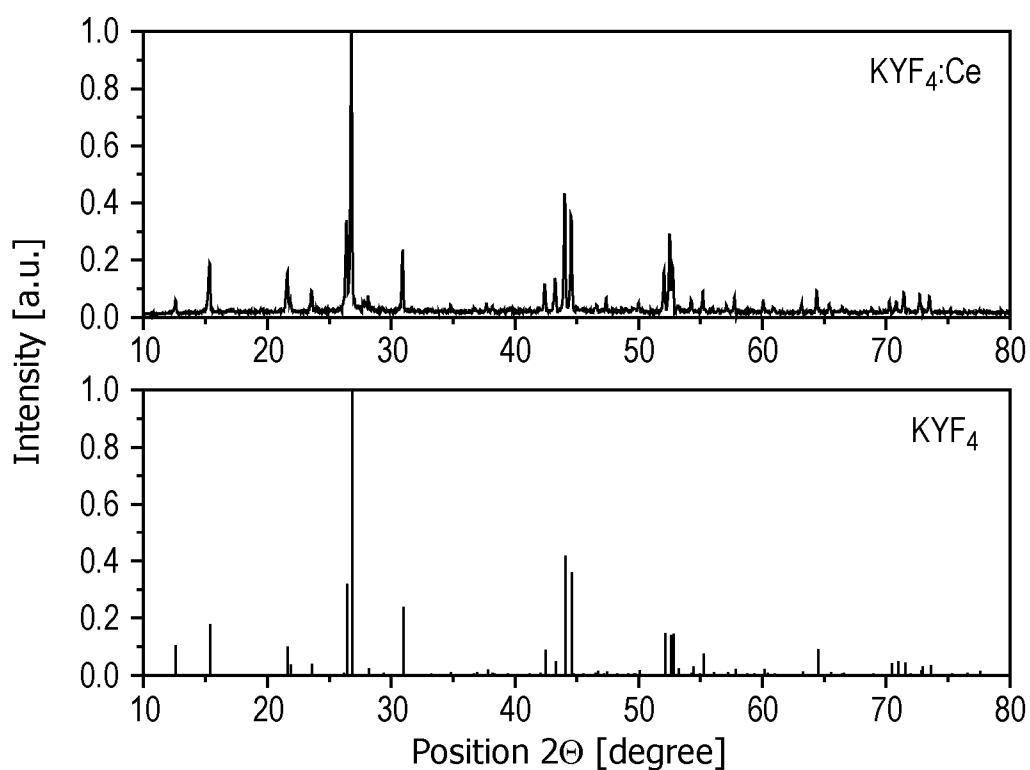


FIG. 2

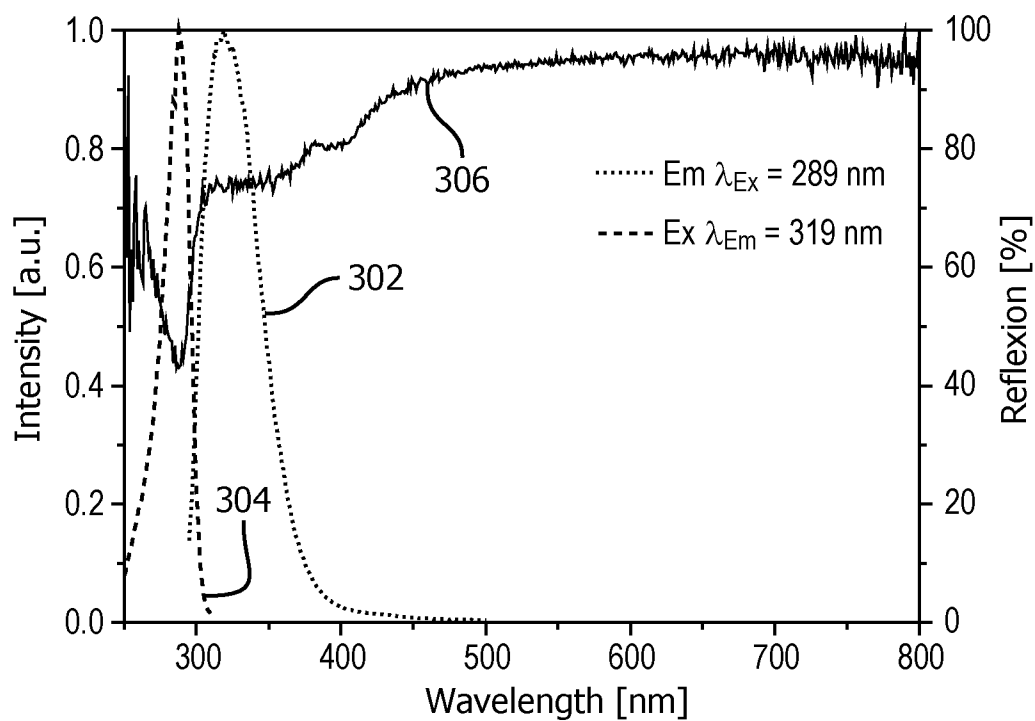


FIG. 3

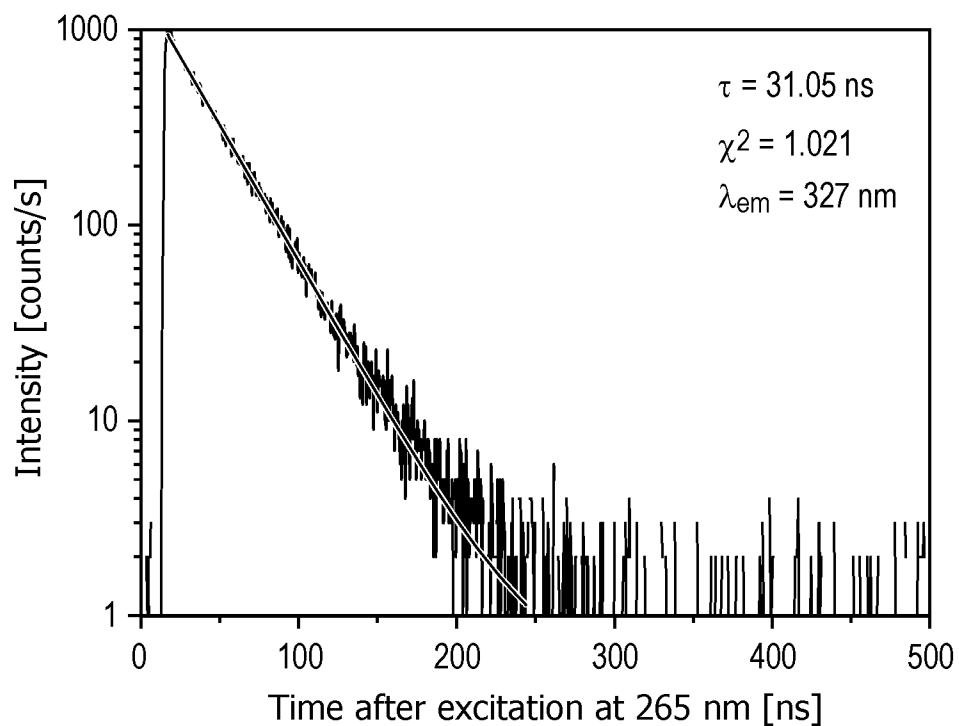


FIG. 4

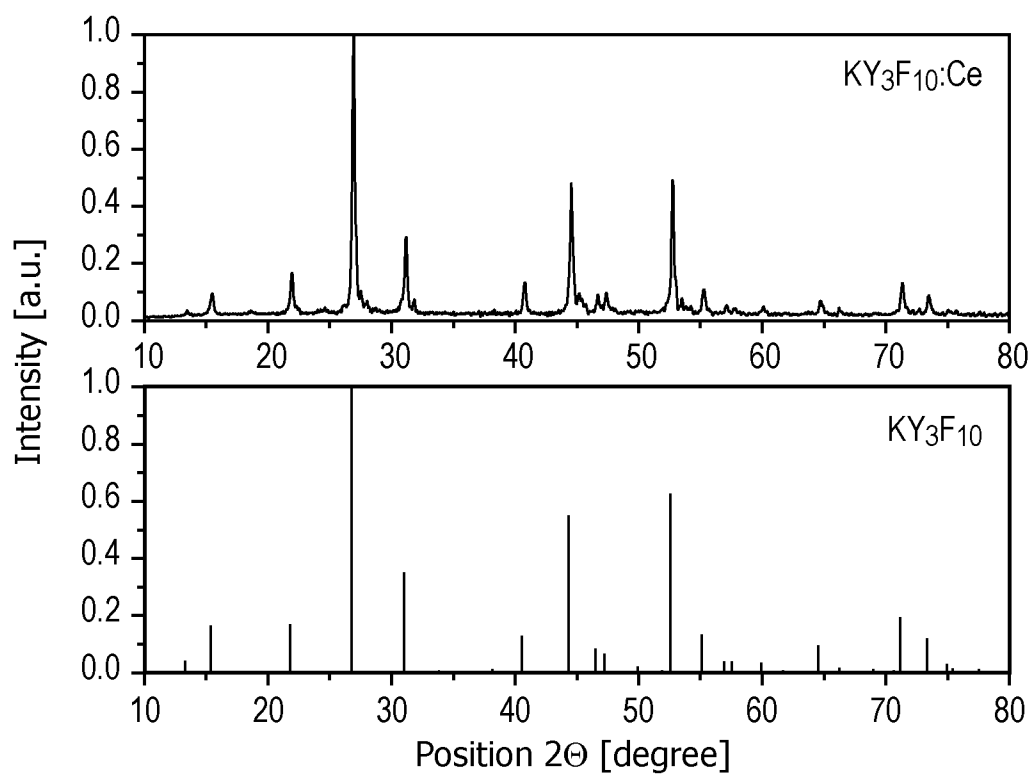


FIG. 5

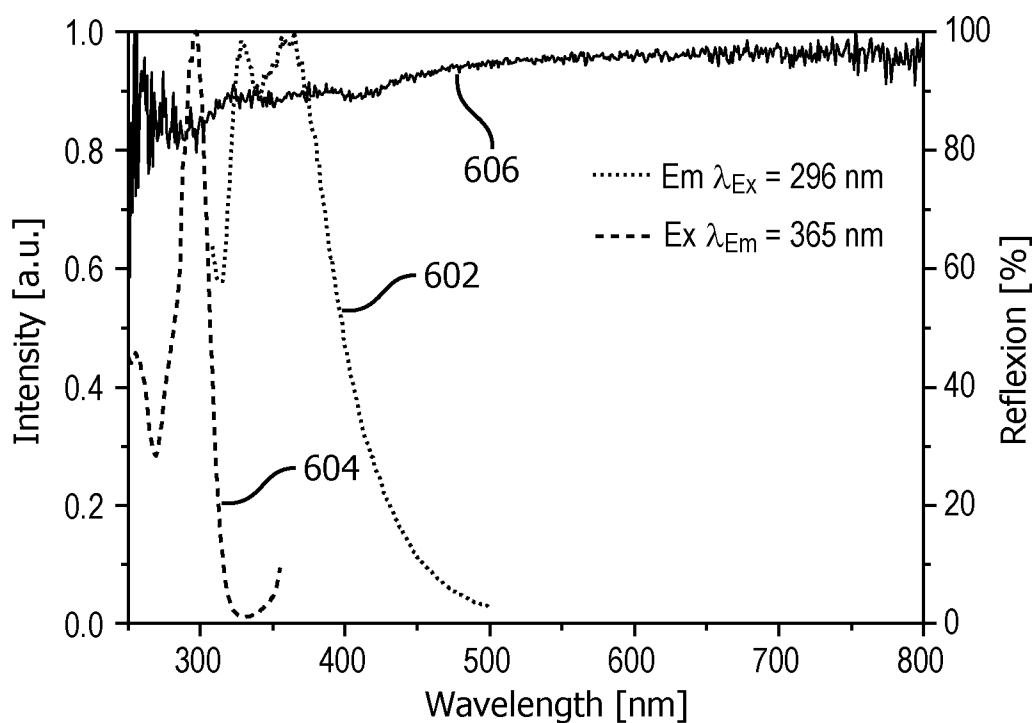


FIG. 6

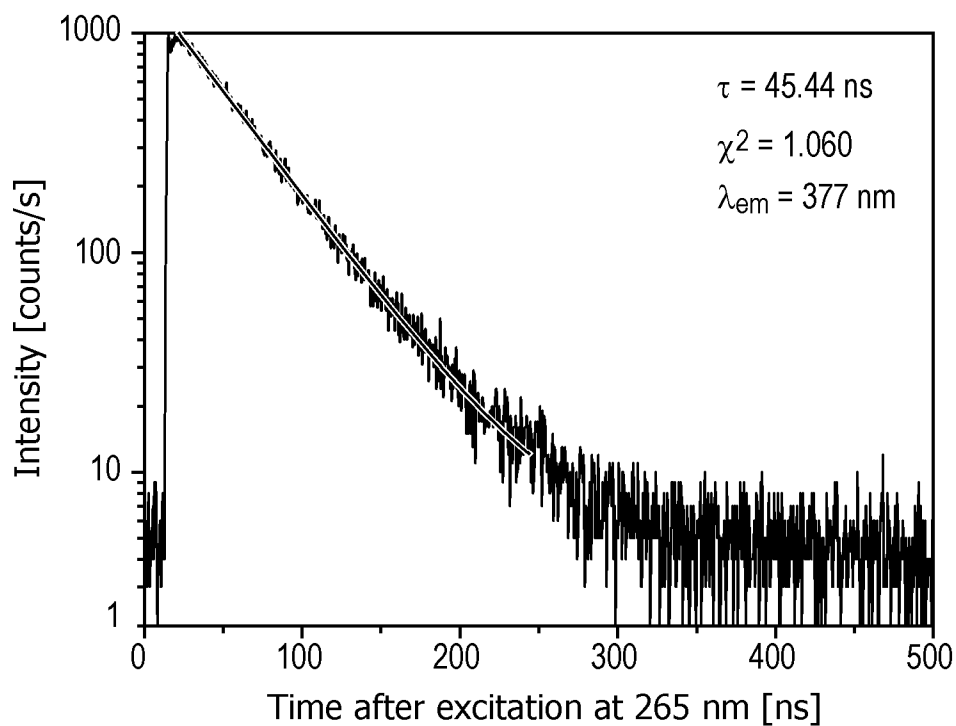


FIG. 7

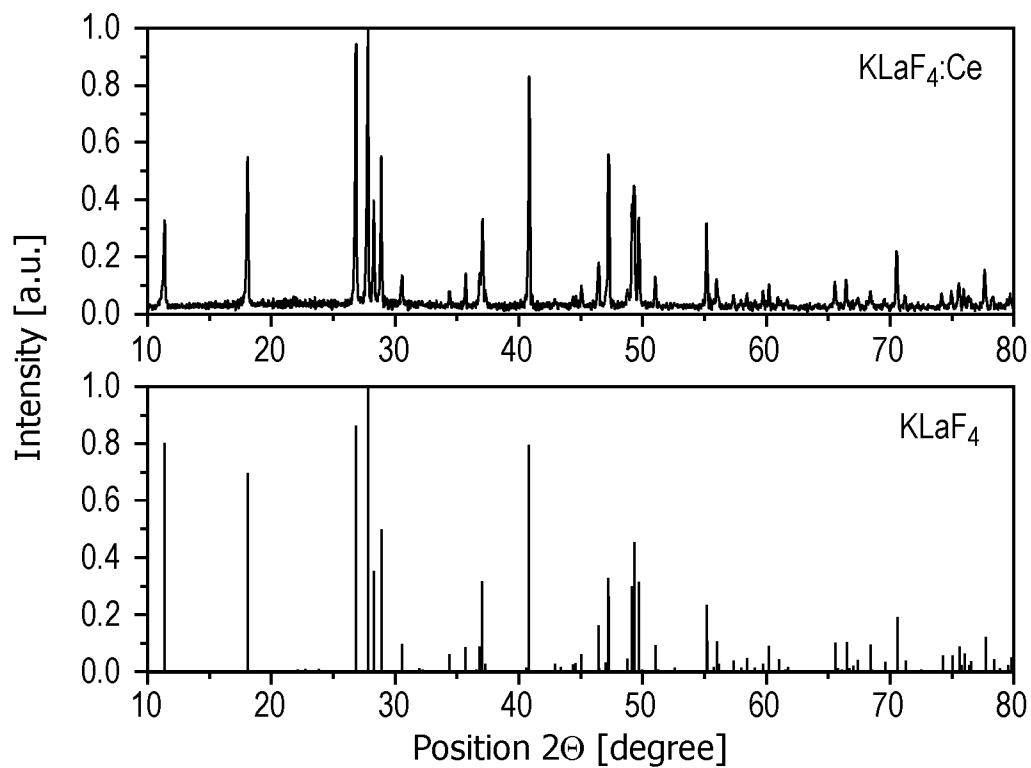


FIG. 8

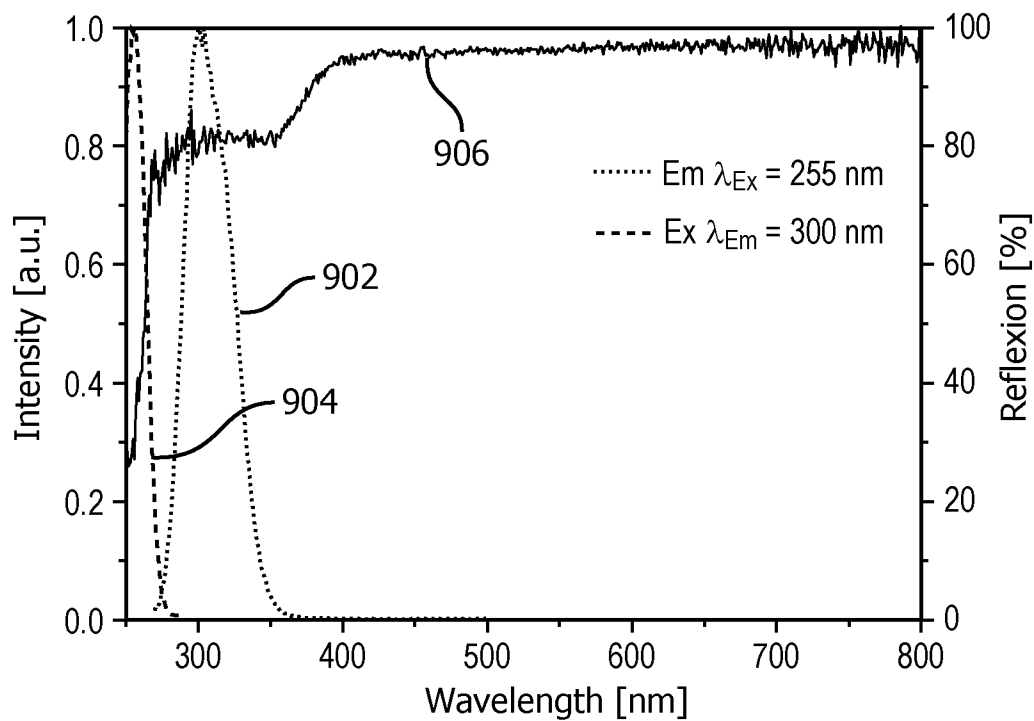


FIG. 9

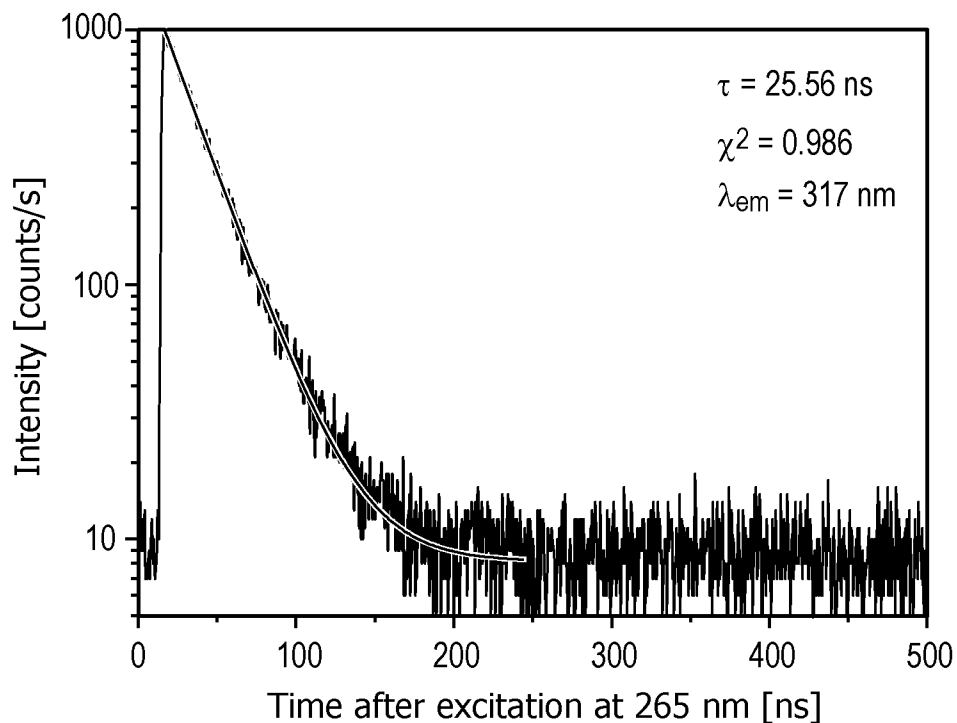


FIG. 10

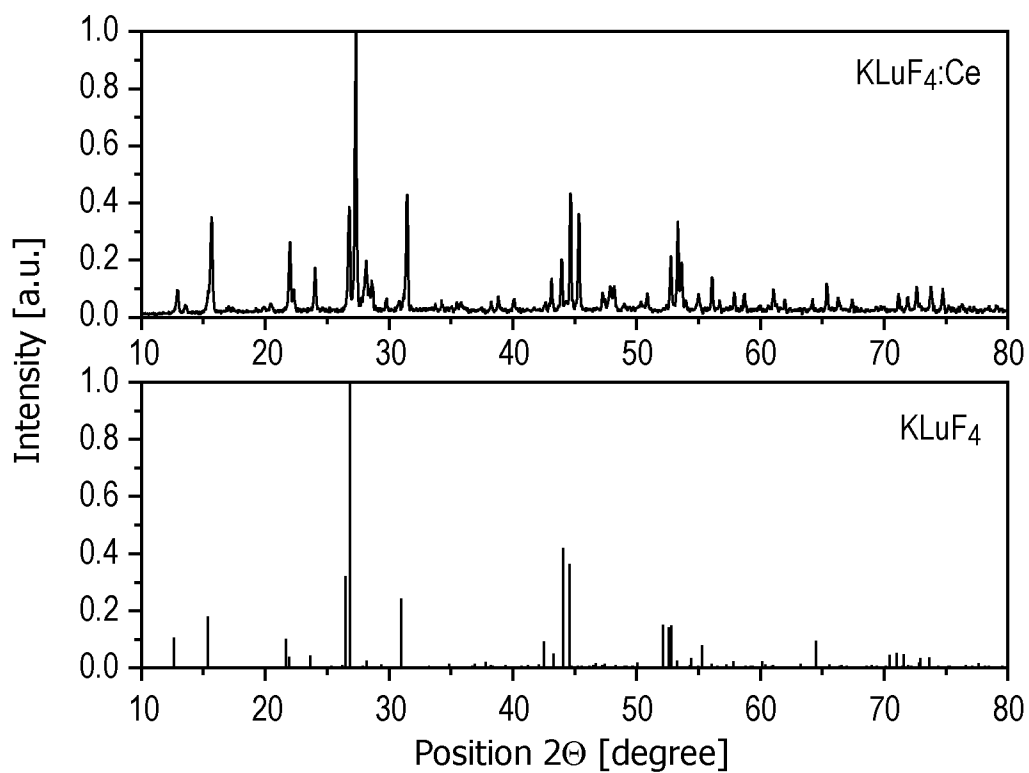


FIG. 11

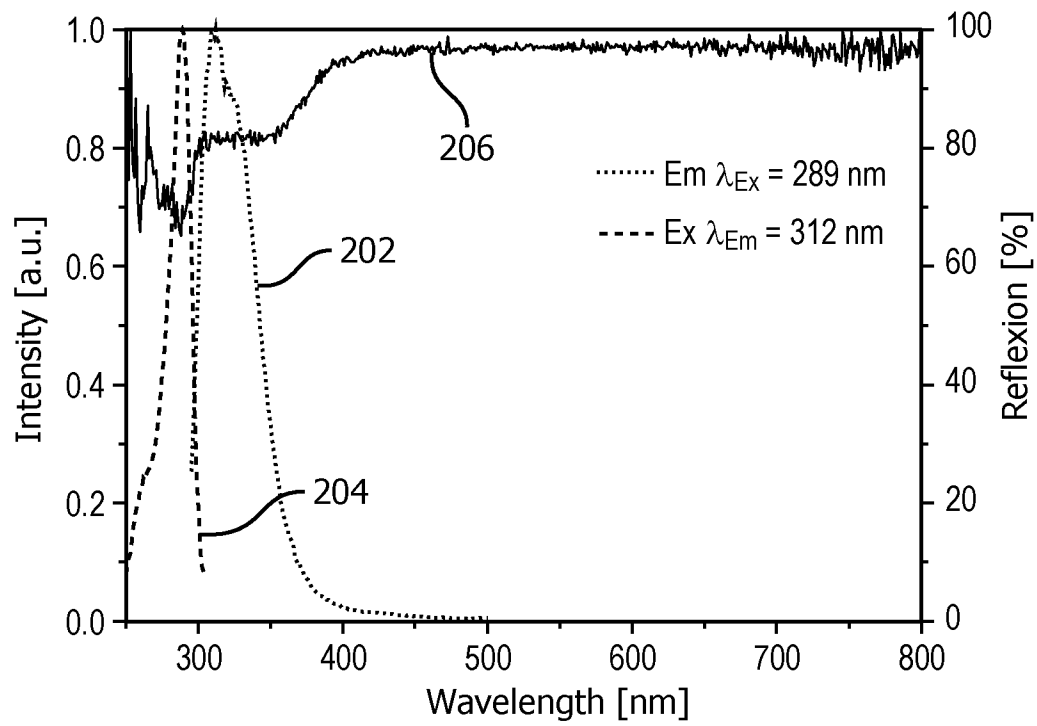


FIG. 12

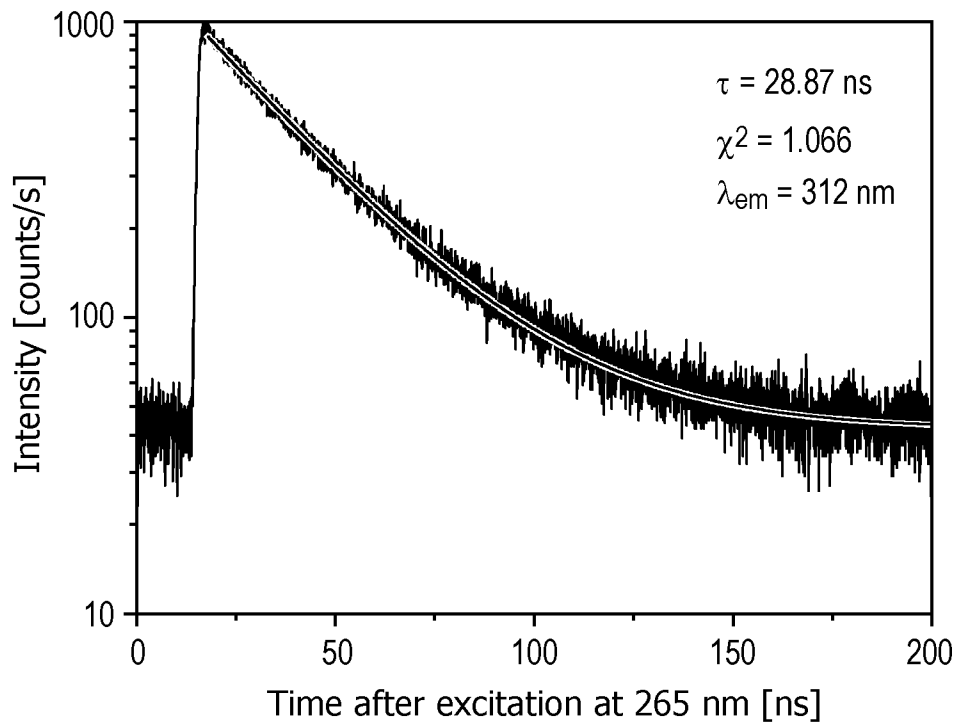


FIG. 13

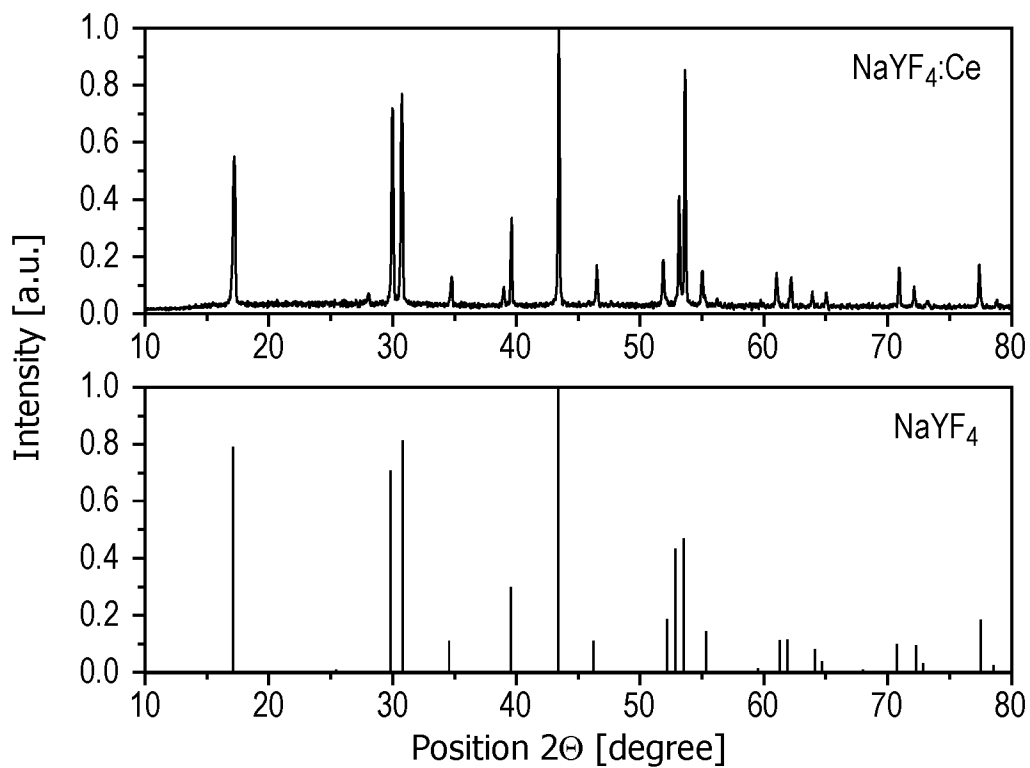


FIG. 14

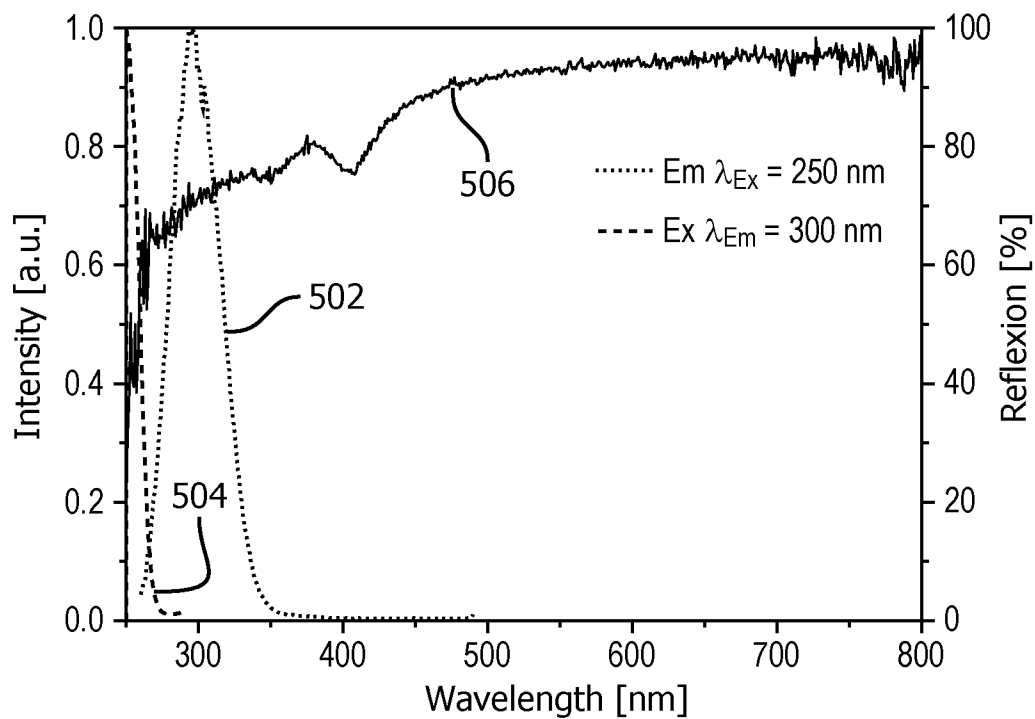


FIG. 15

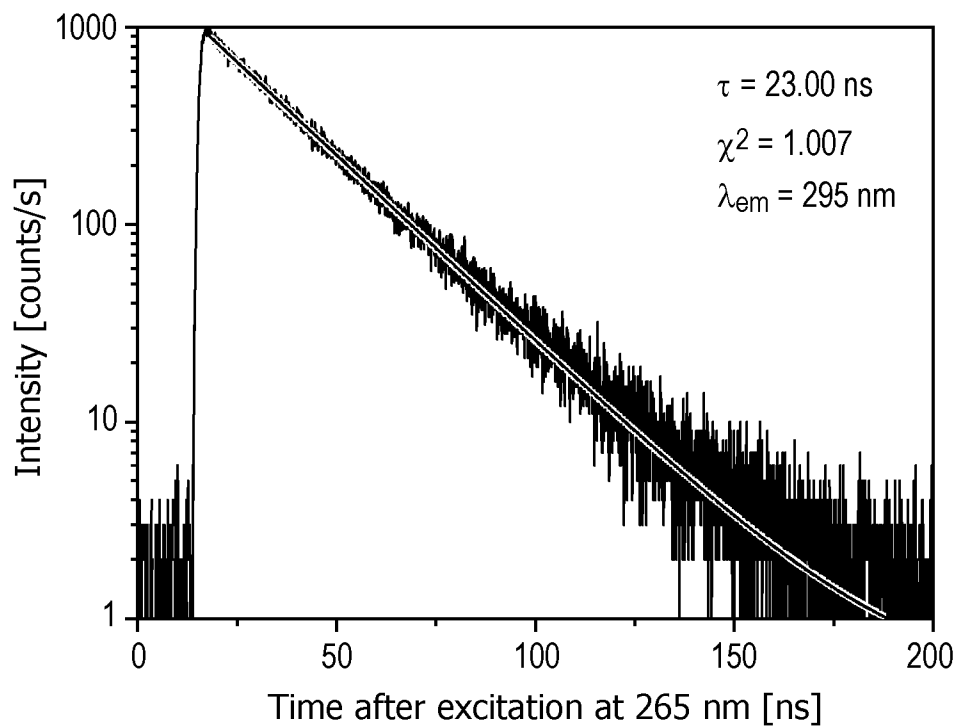


FIG. 16

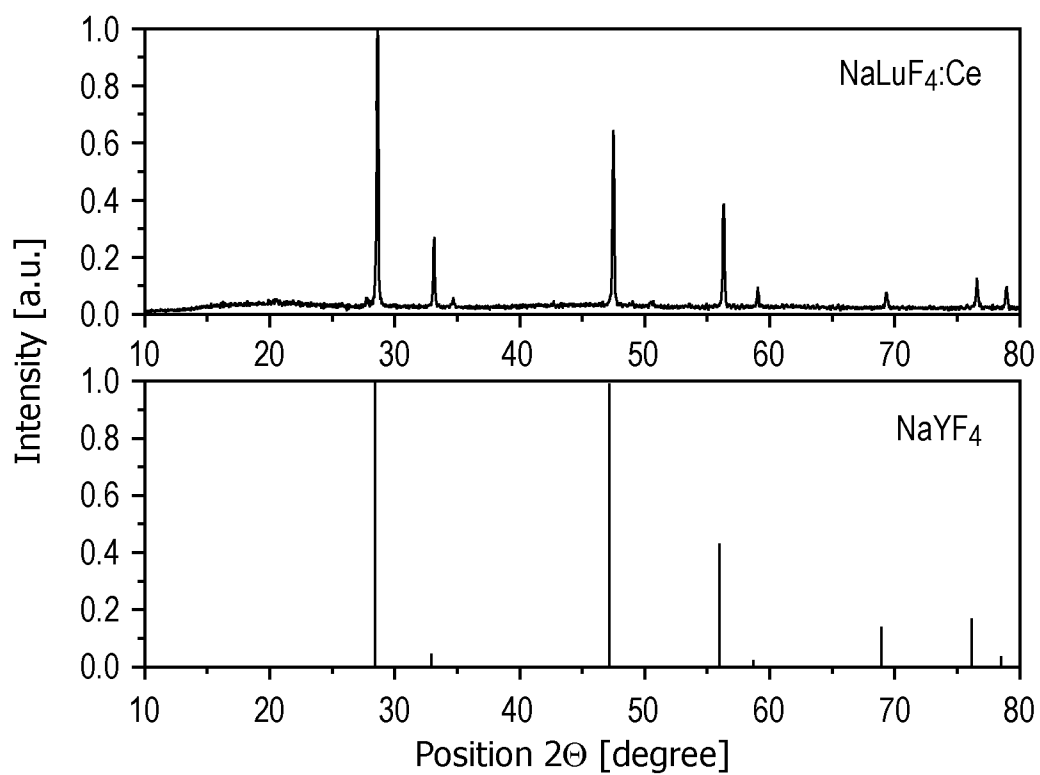


FIG. 17

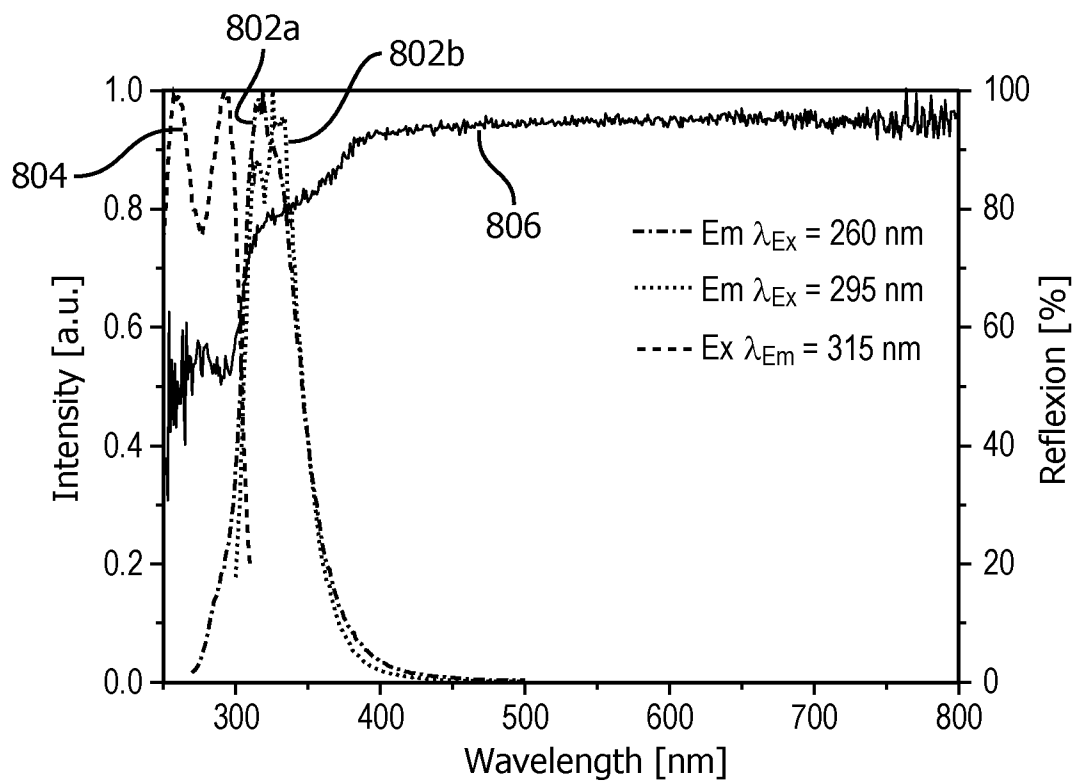


FIG. 18

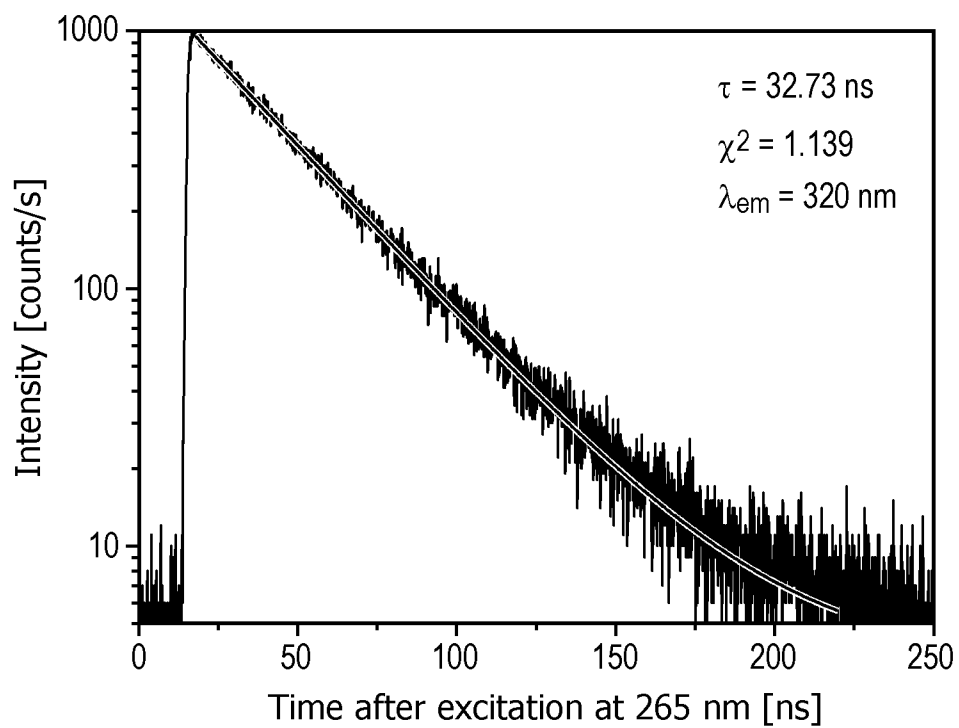


FIG. 19

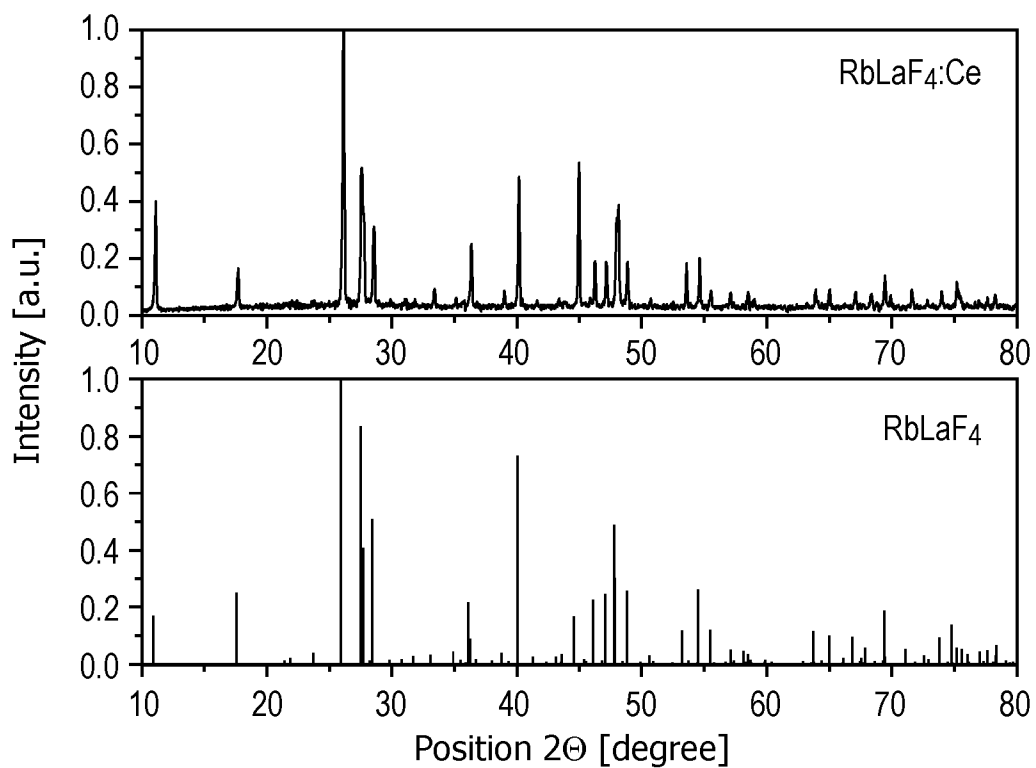


FIG. 20

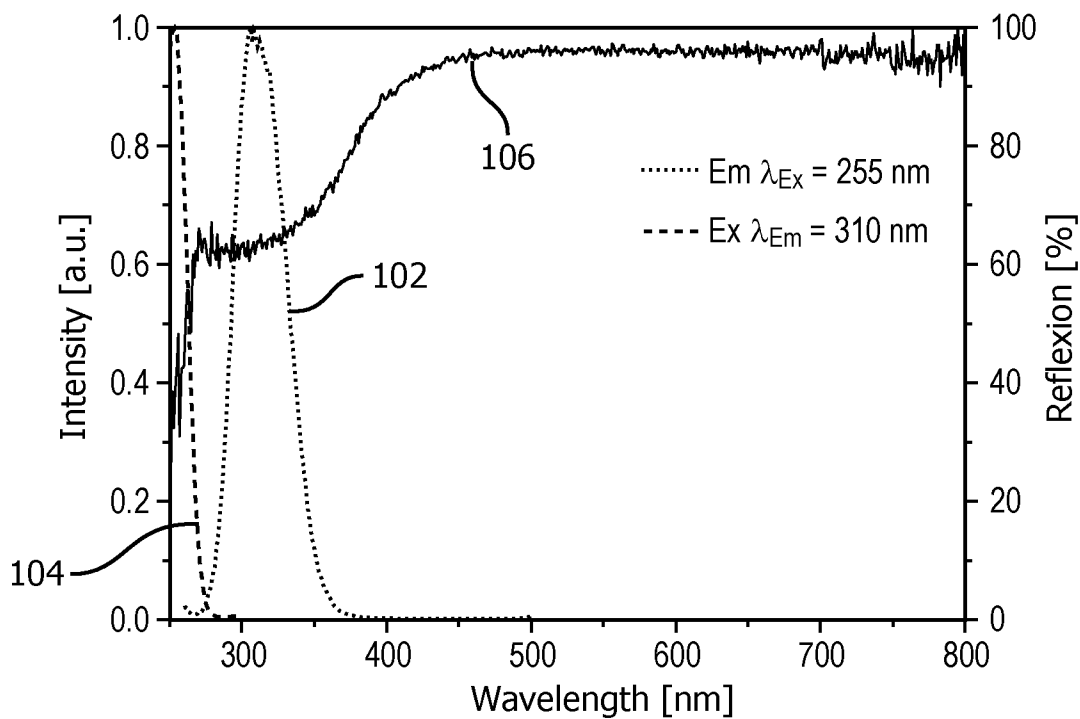


FIG. 21

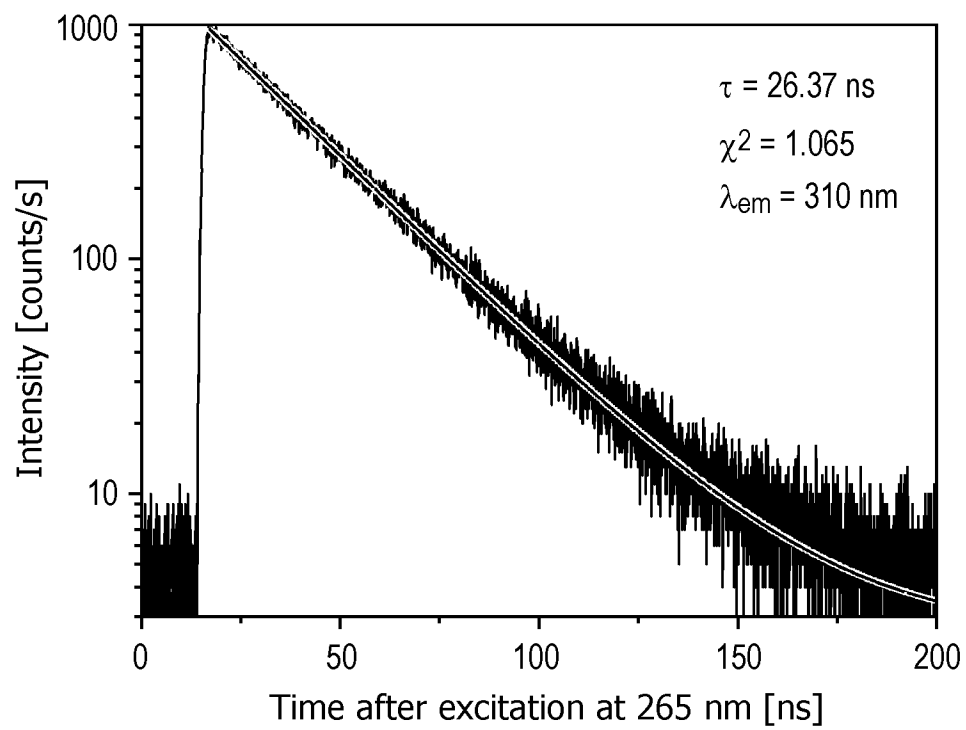


FIG. 22

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2014/063166

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K11/77 G01T1/20
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09K G01T

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2008/213151 A1 (YOSHIKAWA AKIRA [JP] ET AL) 4 September 2008 (2008-09-04) paragraph [0098]; claims 1-101 -----	1-17
X	US 2010/314550 A1 (YOSHIKAWA AKIRA [JP] ET AL) 16 December 2010 (2010-12-16) paragraph [0071]; claims 1-9; examples 4-5 -----	1-17
X	JP 2012 121781 A (TOKUYAMA CORP; UNIV TOHOKU) 28 June 2012 (2012-06-28) paragraph [0001]; claims 1-4 paragraph [0007] - paragraph [0008] ----- -/--	1-17



Further documents are listed in the continuation of Box C.



See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

4 November 2014

Date of mailing of the international search report

12/11/2014

Name and mailing address of the ISA/

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Fax: (+31-70) 340-3016

Authorized officer

Mehdaoui, Imed

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2014/063166

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	J.C VAN 'T SPIJKER ET AL: "Luminescence and scintillation properties of BaY2F8:Ce3+, BaLu2F8 and BaLu2F8:Ce3+", JOURNAL OF LUMINESCENCE, vol. 85, no. 1-3, 1 December 1999 (1999-12-01), pages 11-19, XP055150791, ISSN: 0022-2313, DOI: 10.1016/S0022-2313(99)00154-4 the whole document -----	1-17
X	LING ZHU ET AL: "Facile synthesis and luminescence properties of uniform and monodisperse KY3F10:Ln3+ (Ln=Eu, Ce, Tb) nanospheres", JOURNAL OF LUMINESCENCE, vol. 131, no. 7, 12 March 2011 (2011-03-12), pages 1380-1385, XP055150648, ISSN: 0022-2313, DOI: 10.1016/j.jlumin.2011.03.024 the whole document -----	1-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2014/063166

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2008213151 A1	04-09-2008	CN 102888652 A	23-01-2013
		CN 102888653 A	23-01-2013
		EP 1816241 A1	08-08-2007
		JP 5389328 B2	15-01-2014
		RU 2007121448 A	20-12-2008
		US 2008213151 A1	04-09-2008
		WO 2006049284 A1	11-05-2006

US 2010314550 A1	16-12-2010	CA 2717341 A1	01-10-2009
		CN 101945974 A	12-01-2011
		EP 2256177 A1	01-12-2010
		JP 5378356 B2	25-12-2013
		KR 20100125326 A	30-11-2010
		RU 2010143421 A	27-04-2012
		US 2010314550 A1	16-12-2010
		WO 2009119378 A1	01-10-2009

JP 2012121781 A	28-06-2012	JP 5455881 B2	26-03-2014
		JP 2012121781 A	28-06-2012
