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(54) **Title**: NOVEL SCINTILLATOR MATERIALS FOR NEUTRON DETECTORS

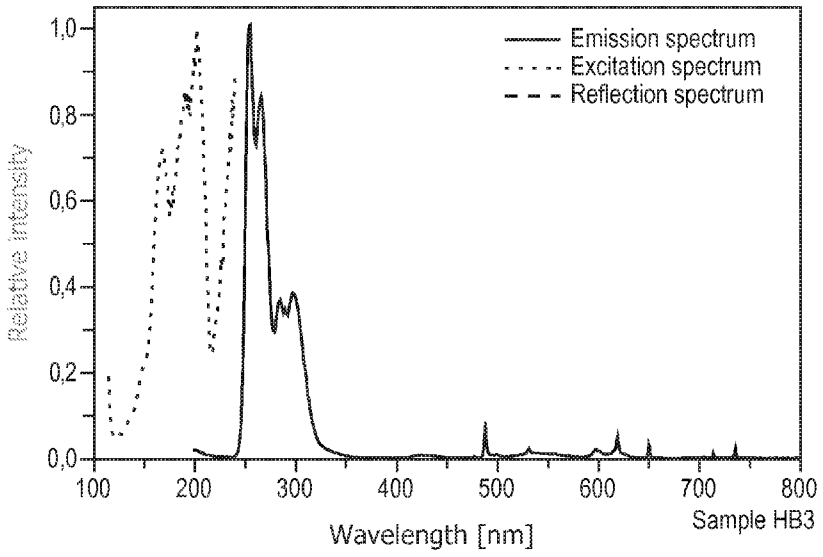

FIG. 1

(57) **Abstract**: This invention relates to novel scintillator materials for neutron detection comprising oxidic and halide rare earth doped lithium- containing materials.

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NOVEL SCINTILLATOR MATERIALS FOR NEUTRON DETECTORS

FIELD OF THE INVENTION

The present invention relates to the field of neutron detectors, especially scintillator materials for neutron detectors.

BACKGROUND OF THE INVENTION

The detection of neutrons is of tremendous interest in the field of nuclear fission and fusion for energy production and for experiments concerning high energy particle physics, e.g. at CERN, DESY, Fermilab etc.

Presently applied materials for the detection of neutrons rely on the nuclear reactions of ^{3}He, ^{6}Li, ^{10}B, or ^{157}Gd with a neutron according to the following equations:

$$n + {}^{3}He \rightarrow {}^{3}H + {}^{1}H + 0.764\ MeV\ \gamma$$

$$n + {}^{6}Li \rightarrow {}^{4}He + {}^{3}H + 4.79\ MeV\ \gamma$$

$$n + {}^{10}B \rightarrow {}^{7}Li^{*} + {}^{4}He \rightarrow {}^{7}Li + {}^{4}He + 0.48\ MeV\ \gamma + 2.3\ MeV\ \gamma$$

$$n + {}^{155}Gd \rightarrow {}^{156}Gd^{*} \rightarrow {}^{156}Gd + \gamma\text{-spectrum}$$

$$n + {}^{157}Gd \rightarrow {}^{158}Gd^{*} \rightarrow {}^{158}Gd + \gamma\text{-spectrum}$$

Most commonly used Li ion comprising materials as neutron scintillators are Ce-doped lithium fluoride glass, LiZnS:LiF, $LiGd(BO_3)_3$:Ce, Rb_2LiYBr_6:Ce, Cs_2LiYCl_6:Ce, and LiI:Eu, whereby the energy efficiency of the scintillation process is between 0.5 and 9% (cf. C. Fouassier et al., Thin Photodiodes for a Neutron Scintillator Silicon-Well Detector, IEEE Trans. Nucl. Sci. 48 (2001) 1154, incorporated by reference) The decay time of these neutron scintillators is in the range of 50 to 500 ns.

In the EP 2 256 177 A1 alternative materials based on rare-earth doped fluorides are disclosed. However, fluorides have the drawback of low melting points, rather low density and a strong tendency of color center formation causing “blackening”, which limits their use in neutron detectors.

Therefore there is still a continuing need for further materials for use as scintillator materials for neutron detection.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide novel scintillator materials for neutron detectors.

This object is solved by a material according to claim 1 of the present invention. Accordingly, a scintillator material for neutron detection is provided, which comprises a material chosen from the group $(Ca,Sr)Li_2(Si,Ge)O_4$:Ln,Me (Ln = Ce, Pr, Nd, Gd; Me = Na, K, Rb, Cs), $RE_9LiSi_6O_{26}$:Ln (RE = Y, La, Lu; Ln = Ce, Pr, Nd, Gd), $Li_6RE(BO_3)_3$:Ln (RE = Y, La, Lu; Ln = Ce, Pr, Nd, Gd), $LiRESiO_4$:Ln (RE = Y, La, Lu; Ln = Ce, Pr, Nd, Gd), $(Sr,Ba)_2Li_2Si_2O_7$:Ln,Me (Ln = Ce, Pr, Nd, Gd; Me = Na, K, Rb, Cs), Li_3RECl_6:Ln (RE = Y, La, Lu; Ln = Ce, Pr, Nd, Gd, $LiREW_2O_8$:RE (RE = Y, La, Lu; Ln = Ce, Pr, Nd, Gd), MX_2: Li, Ce in which M= Ca, Sr Ba and X = Cl, Br or I
or mixtures thereof.

It should be noted that the term "$(Ca,Sr)Li_2(Si,Ge)O_4$:Ln,Me" (or any other chemical composition used in this invention) includes any material which has essentially the desired composition.

The term "essentially" means especially ≥ 95 % preferably ≥ 97 % and most preferred ≥ 99 % wt-%. However, in some applications, trace amounts of additives may also be present in the bulk compositions. These additives particularly include such species known to the art as fluxes. Suitable fluxes include alkaline earth - or alkaline - metal oxides, borates, phosphates and halides such as fluorides, ammonium chloride, SiO_2 and the like and mixtures thereof.

Surprisingly these materials have shown for a wide range of applications within the present invention to have at least one of the following advantages

- The materials have a short decay time, which greatly improves their use for neutron detection
- The materials have a good stability, even under the harsh conditions present in most fields where neutron detectors are used.
- The materials can be pressed into the form of ceramic plates. This enables an additional optimization channel for ^6Li enrichment as the degree of transparency of the ceramics strongly influences the thickness that still can be used. The higher the transparency, the larger the thickness that can be used and

consequently the stronger the neutron absortion will be and lower the concentration of ^{6}Li can be. Alternatively, the detector is not placed behind the scintillator (looking into the propogation direction of the neutrons) but parallel to the length axis of the scintillating unit. In this case also materials can be used with a limited transmittance, but with the same advantage w.r.t. enrichment in ^{6}Li. Moreover and in general, the use of ceramic plates enables the use of structured ceramics, e.g. containing tiny pores, for example perpendicular to the propagation direction of the neutrons, in which Li salts can be incorporated, even in a dissolved state. As shown above, Li is being consumed during operation. An open ceramic structure allows refreshing of the Li-salts. In such a case, the scintillator lattice does not even need to contain any Li.

- ^{6}Li salts can be used a flux agent
- In general, fluorides have large values for the bandgap. This leads to low values for the energy efficiency of the scintilation process. The materials proposed here have much lower band gap values
- In all the rare earth materials mentioned, two trivalent rare earth ion can be substituted by a ^{6}Li ion and a pentavalent ion like Nb^{5+}. This also enables the use of e.g. YBO_3:Ce or even stoichiometric Ce-compounds, i.e. the host lattice chemical formulation does not need to include Li. The level of substitution determines the sensitivity to neutrons.

According to a preferred embodiment of the invention, the materials are ^{6}Li enriched. This has shown for many applications to increase the high absorption cross section for neutrons, since natural Li soley contains 7.5% ^{6}Li. Enrichment especially means and/or includes that the Li^+-sources applied for the synthesis of the Li-scintillator comprise between $\geq$10 and $\leq$50% of ^{6}Li

According to a preferred embodiment of the invention the rare earth material doping level is $\geq$0.1% and $\leq$20%. This has shown to be advantageous for most applications. Preferably the the rare earth material doping level is $\geq$1% and $\leq$10%.

The present invention furthermore relates to a neutron intensifying screen comprising at least one material according to the present invention

The present invention furthermore relates to the use of a material comprising a material chosen from the group $(Ca,Sr)Li_2(Si,Ge)O_4$:Ln,Me (Ln = Ce, Pr, Nd, Gd; Me = Na, K, Rb, Cs), $RE_9LiSi_6O_{26}$:Ln (RE = Y, La, Lu; Ln = Ce, Pr, Nd, Gd), $Li_6RE(BO_3)_3$:Ln (RE =

Y, La, Lu; Ln = Ce, Pr, Nd, Gd), $LiRESiO_4$:Ln (RE = Y, La, Lu; Ln = Ce, Pr, Nd, Gd), $(Sr,Ba)_2Li_2Si_2O_7$:Ln,Me (Ln = Ce, Pr, Nd, Gd; Me = Na, K, Rb, Cs), Li_3RECl_6:Ln (RE = Y, La, Lu; Ln = Ce, Pr, Nd, Gd, $LiREW_2O_8$:RE (RE = Y, La, Lu; Ln = Ce, Pr, Nd, Gd), MX_2:Li, Ce in which M = Ca, Sr Ba and X = Cl, Br or I

or mixtures thereof for neutron detection.

The present invention furthermore relates to as system comprising a material and/or a neutron intensifying screen and/or according to the inventive use shown above, being used in one or more of the following applications:

- neutron detection
- elementary particle physics
- fission reactors

The aforementioned components, as well as the claimed components and the components to be used in accordance with the invention in the described embodiments, are not subject to any special exceptions with respect to their size, shape, material selection and technical concept such that the selection criteria known in the pertinent field can be applied without limitations.

BRIEF DESCRIPTION OF THE DRAWINGS

Additional details, features, characteristics and advantages of the object of the invention are disclosed in the subclaims, the figures and the following description of the respective figures and examples, which -- in an exemplary fashion-- show several embodiments and examples of inventive materials according to the invention.

Fig. 1 shows a diagram depicting the excitation and emission spectra of the material according to Example I

Fig. 2 shows a diagram depicting the decay curve of the material according to Example I

Fig. 3 shows the XRD pattern of the material according to Example I

Fig. 4 shows a diagram depicting the excitation and emission spectra of the material according to Example II

Fig. 5 shows a diagram depicting the decay curve of the material according to Example II

Fig. 6 shows the XRD pattern of the material according to Example II

Fig. 7 shows a diagram depicting the excitation and emission spectra of the material according to Example III

Fig.8 shows the XRD pattern of the material according to Example III

EXAMPLE I

The invention will further be understood by the following Example I which is merely for illustration and which is non-binding.

Example I relates to $CaLi_2SiO_4:Pr^{3+}Na^+$ which was made the following way:

25.00 g (277.87 mmol) Li_2SiO_3, 0.147 g (1.38 mmol) Na_2CO_3, 27.256 g (272.31mmol) $CaCO_3$, and 1.209 (2.87 mmol) $Pr(NO_3)_3{\cdot}6H_2O$ are mixed by slurring in demi H_2O. The water is subsequently removed by evaporation. After drying, the powder is fired in air for 2 hrs at 700 °C. Thereafter, the material is fired twice at 850 °C in a CO atmosphere.

The resulting greenish-white material is then washed with water and ethanol, dried, milled on a roller bench for several hours, and finally sieved through a 36 μm sieve.

The gained powder has an average particle size of 3 μm.

Fig. 1 shows the excitation (dotted line) and emission spectra (solid line) of the material of Example I. Fig. 2 shows the decay curve of Example I ($\tau_{1/e}$ = 16 ns monitored for the 255 nm emission band), Fig. 3 the XRD pattern. From the figures it can clearly be seen that this material is an excellent material for neutron detection scintillators.

EXAMPLE II

Example II relates to $CaLi_2SiO_4$:CeNa which was made the following way:

8.996 g (100 mmol) Li_2SiO_3, 0.106 g (1.0 mmol) Na_2CO_3, 9.608 g (96.0 mmol) $CaCO_3$, and 0.869 (2.0 mmol) $Ce(NO_3)_3{\cdot}6H_2O$ are mixed by slurring in demi H_2O. The water is subsequently removed by evaporation. After drying, the powder is fired in air for 2 hrs at 700°C. Thereafter, the material is fired for 48 hrs at 900°C in a N_2/H_2 (95/5) atmosphere

The resulting pure-white material is then washed with water and ethanol, dried, milled on a roller bench for several hours, and finally sieved through a 36 μm sieve. The gained powder has an average particle size of 3 μm.

Fig. 4 shows the excitation (dotted line) and emission spectra (solid line) of the material of Example I. Fig. 5 shows the decay curve of Example I ($\tau_{1/e}$ = 36 ns monitored for the 405 nm emission band), Fig. 6 the XRD pattern. From the figures it can clearly be seen that this material is an excellent material for neutron detection scintillators.

EXAMPLE III

Example III relates to $CaLi_2SiO_4$:Nd,Na which was made the following way: 25.00 g (277.87 mmol) Li_2SiO_3, 0.147 g (1.38 mmol) Na_2CO_3, 27.256 g (272.31mmol) $CaCO_3$, and 1.211 (2.87 mmol) $Nd(NO_3)_3 \cdot 6H_2O$ are mixed by slurring in demi H_2O. The water is subsequently removed by evaporation. After drying, the powder is fired in air for 2 hrs at 700 °C. Thereafter, the material is twice fired at 850 °C in a CO atmosphere.

The resulting greenish-white material is then washed with water and ethanol, dried, milled on a roller bench for several hours, and finally sieved through a 36 μm sieve. The gained powder has an average particle size of 4 μm.

Fig. 7 shows the excitation (dotted line) and emission spectra (solid line) of the material of Example I, Fig. 8 the XRD pattern. From the figures it can clearly be seen that this material is an excellent material for neutron detection scintillators

FURTHER EXAMPLES

The decay times and emission maxima of further inventive materials were measured and are depicted in Table I

TABLE I

Material	**τ (ns)**	**λ_{max} (nm)**
$LuPO_4$:Pr	10	235
$LuBO_3$:Pr	13	255
YBO_3:Pr	15	260
Lu_2SiO_5:Pr	16	270
$Lu_2Si_2O_7$:Pr	17	270
$Ba_2Y_2Si_4O_{13}$:Pr	18	275
$Y_9LiSi_6O_{26}$:Pr	20	275
$Lu_3Al_5O_{12}$:Pr	24	310
$Ca_3Sc_2Si_3O_{12}$:Pr	26	323

The particular combinations of elements and features in the above detailed embodiments are exemplary only; the interchanging and substitution of these teachings with other teachings in this and the patents/applications incorporated by reference are also expressly contemplated. As those skilled in the art will recognize, variations, modifications, and other implementations of what is described herein can occur to those of ordinary skill in the art without departing from the spirit and the scope of the invention as claimed.

Accordingly, the foregoing description is by way of example only and is not intended as limiting. In the claims, the word "comprising" does not exclude other elements or steps, and the indefinite article "a" or "an" does not exclude a plurality. The mere fact that certain measures are recited in mutually different dependent claims does not indicate that a combination of these measured cannot be used to advantage. The invention's scope is defined in the following claims and the equivalents thereto. Furthermore, reference signs used in the description and claims do not limit the scope of the invention as claimed.

CLAIMS:

1. A scintillator material for neutron detection comprising a material chosen from the group $(Ca,Sr)Li_2(Si,Ge)O_4$:Ln,Me (Ln = Ce, Pr, Nd, Gd; Me = Na, K, Rb, Cs), $RE_9LiSi_6O_{26}$:Ln (RE = Y, La, Lu; Ln = Ce, Pr, Nd, Gd), $Li_6RE(BO_3)_3$:Ln (RE = Y, La, Lu; Ln = Ce, Pr, Nd, Gd), $LiRESiO_4$:Ln (RE = Y, La, Lu; Ln = Ce, Pr, Nd, Gd), $(Sr,Ba)_2Li_2Si_2O_7$:Ln,Me (Ln = Ce, Pr, Nd, Gd; Me = Na, K, Rb, Cs), Li_3RECl_6:Ln (RE = Y, La, Lu; Ln = Ce, Pr, Nd, Gd, $LiREW_2O_8$:RE (RE = Y, La, Lu; Ln = Ce, Pr, Nd, Gd), MX_2: Li, Ce in which M = Ca, Sr Ba and X = Cl, Br or I

or mixtures thereof

2. The material of claim 1, whereby the material is ^6Li enriched.

3. The material of claim 1 or 2, whereby the rare earth material dotation level is ≥0.1% and ≤30%

4. A neutron intensifying screen comprising at least one material according to any of the claims 1 to 3.

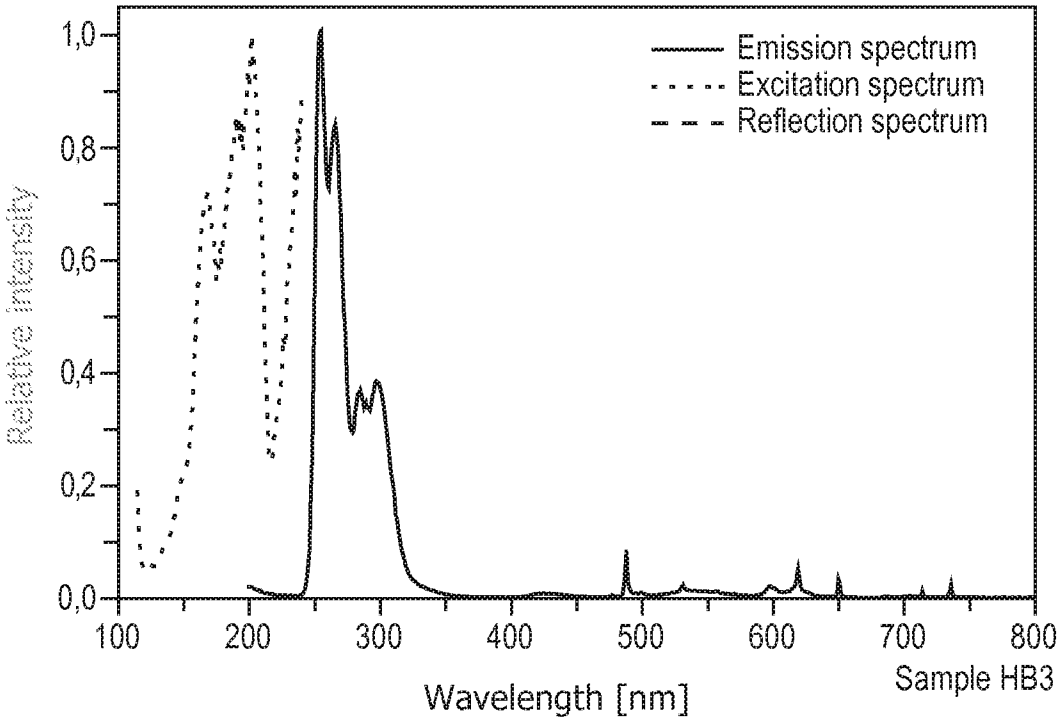
5. Use of a material comprising a material chosen from the group $(Ca,Sr)Li_2(Si,Ge)O_4$:Ln,Me (Ln = Ce, Pr, Nd, Gd; Me = Na, K, Rb, Cs), $RE_9LiSi_6O_{26}$:Ln (RE = Y, La, Lu; Ln = Ce, Pr, Nd, Gd), $Li_6RE(BO_3)_3$:Ln (RE = Y, La, Lu; Ln = Ce, Pr, Nd, Gd), $LiRESiO_4$:Ln (RE = Y, La, Lu; Ln = Ce, Pr, Nd, Gd), $(Sr,Ba)_2Li_2Si_2O_7$:Ln,Me (Ln = Ce, Pr, Nd, Gd; Me = Na, K, Rb, Cs), Li_3RECl_6:Ln (RE = Y, La, Lu; Ln = Ce, Pr, Nd, Gd, $LiREW_2O_8$:RE (RE = Y, La, Lu; Ln = Ce, Pr, Nd, Gd), MX_2: Li,Ce in which M= Ca, Sr Ba and X = Cl, Br or I

or mixtures thereof for neutron detection

6. The use of claim 5, whereby the material is ^6Li enriched.

7. A system comprising a material according to any of the claims 1 to 3 and/or a screen according to claim 4 and/or making use of claim 5 or 6, the system being used in one or more of the following applications:

- neutron detection
- elementary particle physics
- fission reactors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Excitation spectrum
Reflection spectrum
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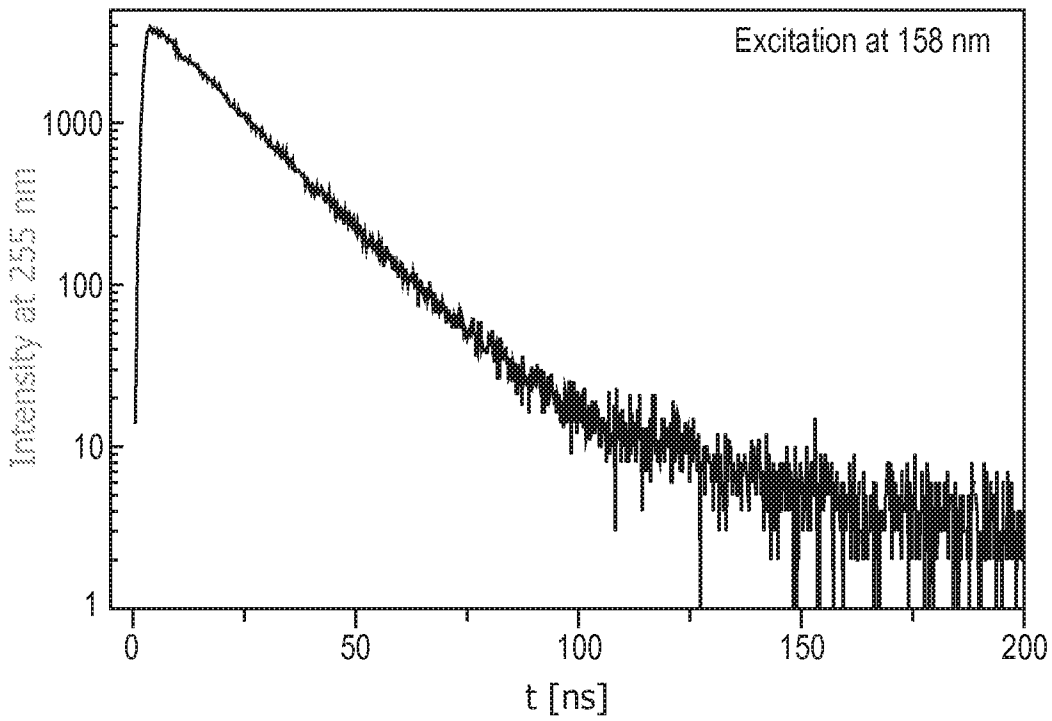
500
600
700
800
Wavelength [nm]
Sample HB3

FIG. 1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Intensity at 255 nm
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50
100
150
200
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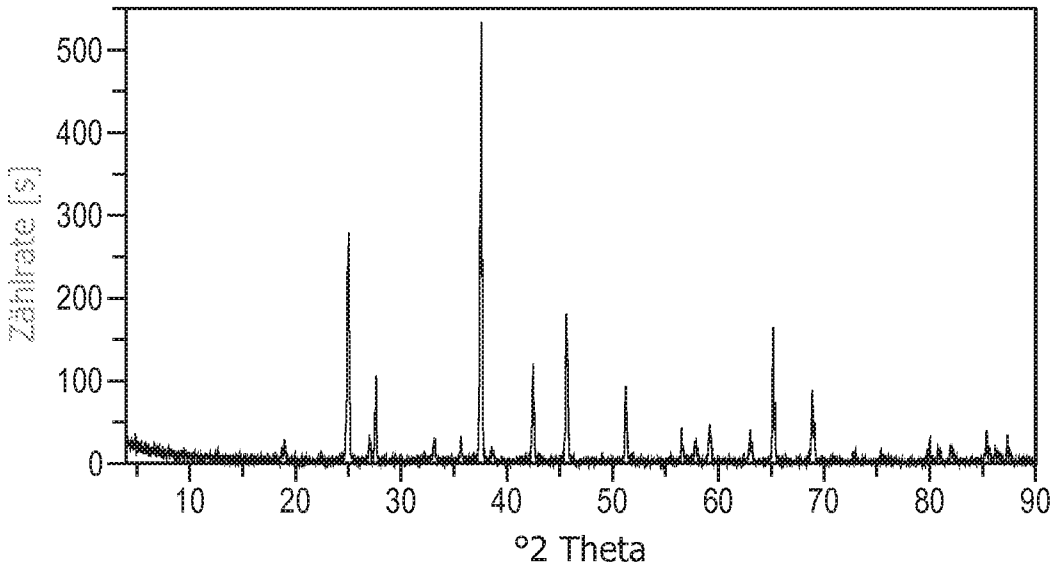
FIG. 2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70
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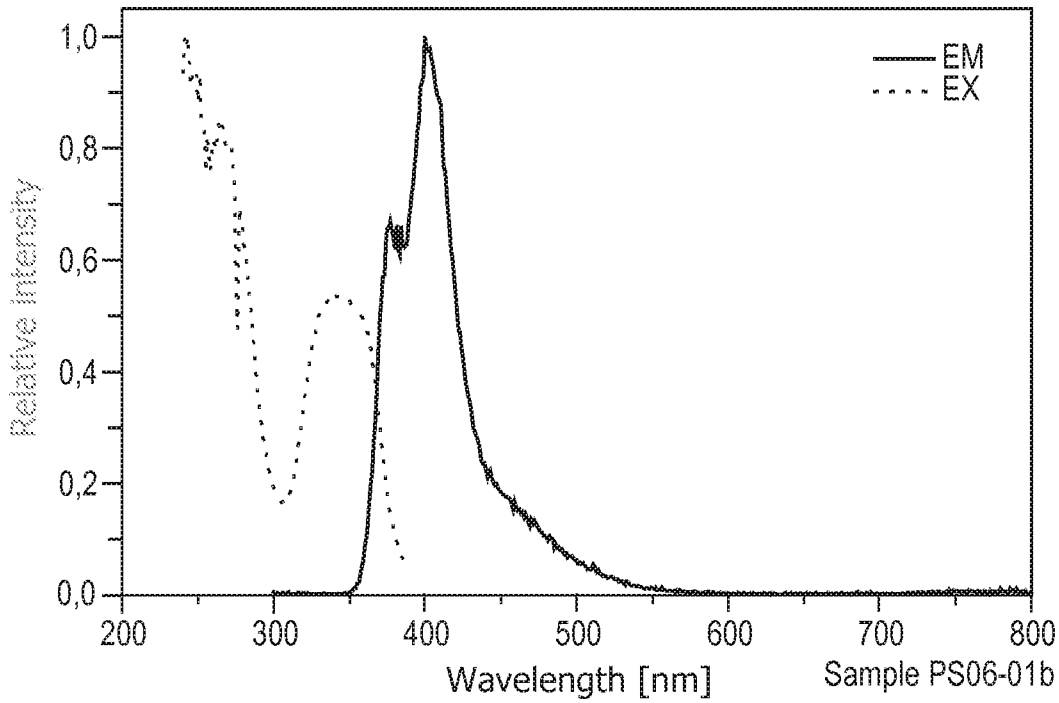
°2 Theta

FIG. 3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0,4
0,2
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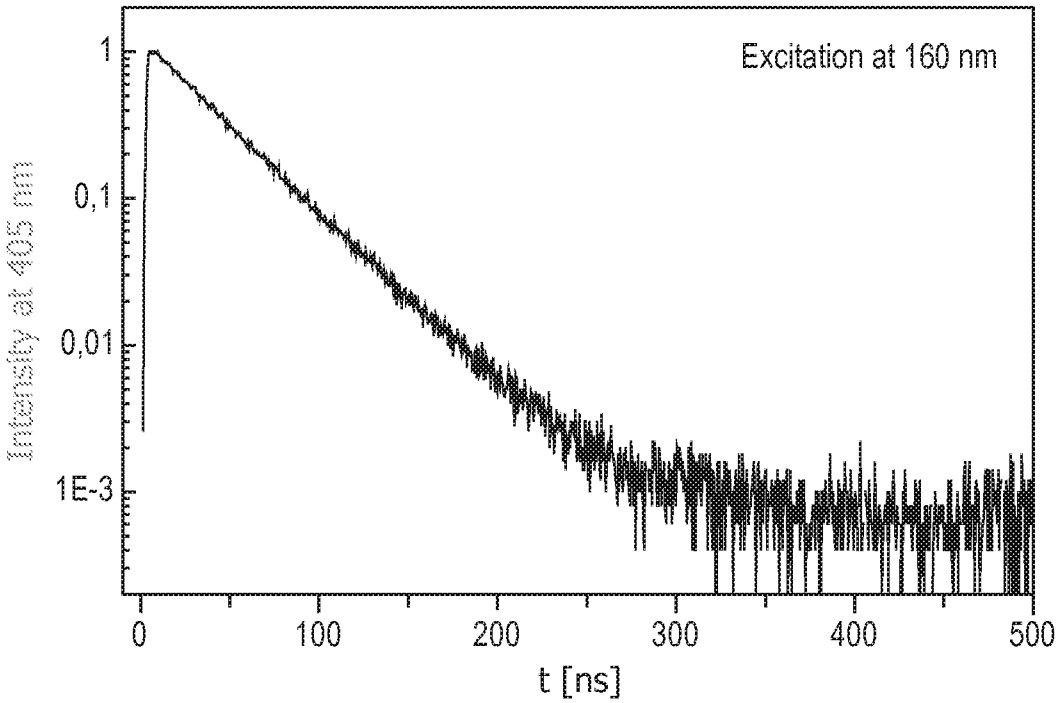
800
Wavelength [nm]
EM
EX
Sample PS06-01b

FIG. 4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Intensity at 405 nm
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100
200
300
400
500
t [ns]

FIG. 5

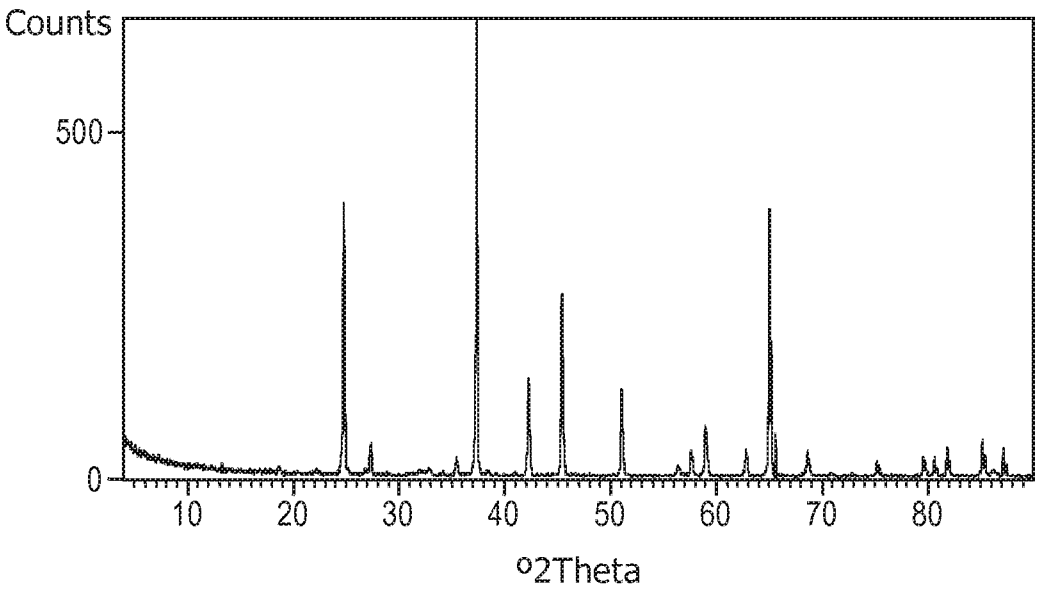
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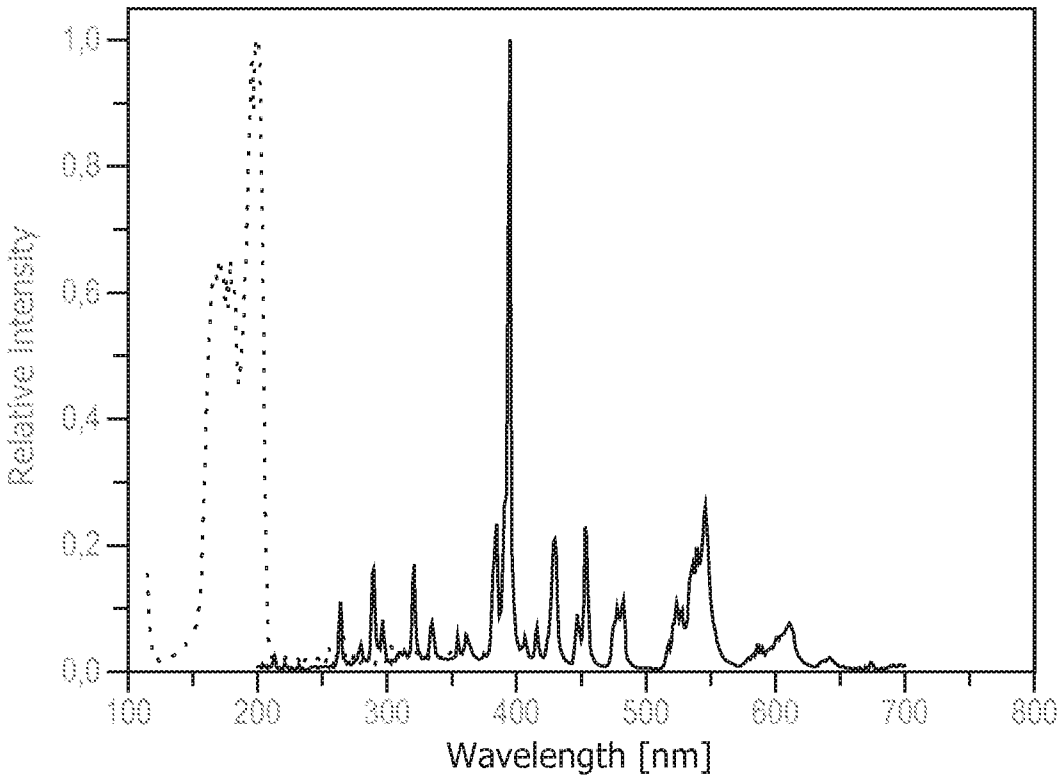
FIG. 6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100
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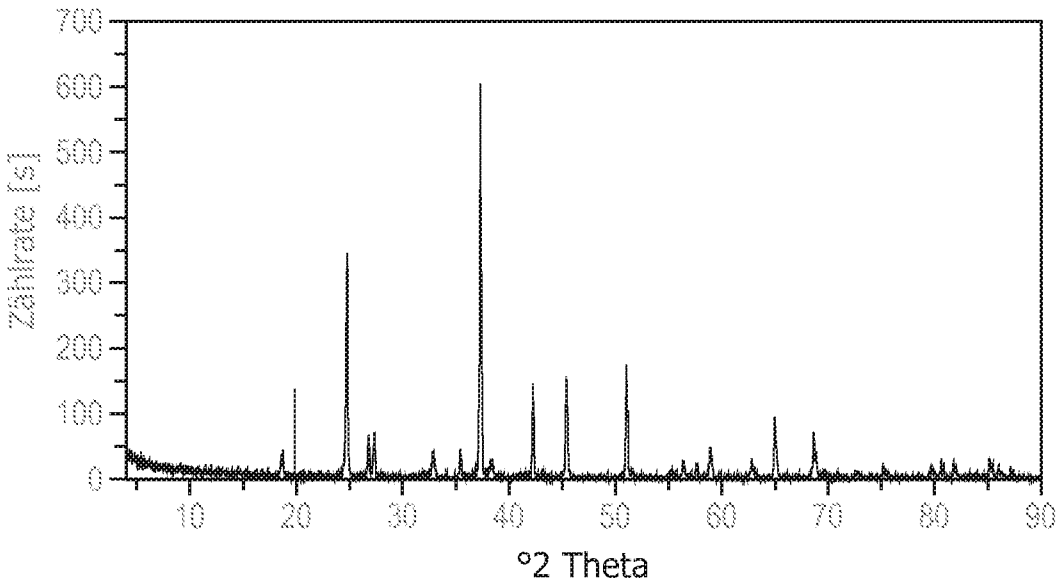
Wavelength [nm]

FIG. 7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60
70
80
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°2 Theta

FIG. 8