(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 212 400 B9

(12) CORRECTED EUROPEAN PATENT SPECIFICATION

(15) Correction information:
Corrected version no 1 (W1 B1)
Corrections, see
Claims EN 1

(48) Corrigendum issued on:
16.04.2014 Bulletin 2014/16

(45) Date of publication and mention of the grant of the patent:
26.12.2012 Bulletin 2012/52

(21) Application number: **08838709.7**

(22) Date of filing: **14.10.2008**

(51) Int Cl.:
C09K 11/08 (2006.01) ***C09K 11/79*** (2006.01)
C09K 11/80 (2006.01)

(86) International application number:
PCT/EP2008/063810

(87) International publication number:
WO 2009/050171 (23.04.2009 Gazette 2009/17)

(54) RARE-EARTH DOPED ALKALINE-EARTH SILICON NITRIDE PHOSPHOR, METHOD FOR PRODUCING AND RADIATION CONVERTING DEVICE COMPRISING SUCH A PHOSPHOR

SE-DOTIERTER ERDALKALISILICIUMNITRIDLEUCHTSTOFF, VERFAHREN ZUR HERSTELLUNG UND EINEN DERARTIGEN LEUCHTSTOFF UMFASSENDE STRAHLUNGSKONVERTIERUNGSVORRICHTUNG

PHOSPHORE DE NITRURE DE SILICIUM ALCALINO-TERREUX DOPÉ AUX TERRES RARES, PROCÉDÉ DE PRODUCTION ET DISPOSITIF DE CONVERSION DES RAYONNEMENTS COMPRENANT UN TEL PHOSPHORE

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MT NL NO PL PT RO SE SI SK TR

(30) Priority: **15.10.2007 EP 07118436**

(43) Date of publication of application:
04.08.2010 Bulletin 2010/31

(73) Proprietors:
- **Leuchtstoffwerk Breitungen GmbH**
  98597 Breitungen (DE)
- **Tridonic Jennersdorf GmbH**
  8380 Jennersdorf (AT)

(72) Inventors:
- **DUAN, Cheng-Jun**
  36433 Bad Salzungen (DE)
- **HINTZEN, Hubertus Theresia**
  NL-5646 JE Eindhoven (NL)
- **RÖSLER, Sylke**
  99817 Eisenach (DE)
- **STARICK, Detlef**
  17489 Greifswald (DE)
- **RÖSLER, Sven**
  99817 Eisenach (DE)
- **DELSING, Anne Charlotte Anoinette**
  NL-5616 HZ Eindhoven (NL)

(74) Representative: **Engel, Christoph Klaus**
Engel Patentanwaltskanzlei
Marktplatz 6
98527 Suhl/Thüringen (DE)

(56) References cited:
EP-A- 1 104 799
WO-A-2005/083037
WO-A-2006/126567
US-A1- 2007 114 548

EP 2 212 400 B9

Description

FIELD OF THE INVENTION

[0001] This invention relates to a method of manufacturing a rare-earth doped alkaline-earth silicon nitride phosphor. Said method comprising the step of selecting one or more compounds each comprising at least one element of the group comprising the rare-earths elements (RE), the alkaline-earth elements (AE), silicon (Si) and nitrogen (N) and together comprising the necessary elements to form the rare earth doped alkaline earth silicon nitride phosphor ($AE_2Si_5N_8$:RE). A further step of the method is bringing the compounds at an elevated temperature in reaction for forming the rare-earth doped alkaline-earth silicon nitride phosphor ($AE_2Si_5N_8$:RE), whereby a small amount of oxygen, whether intentionally or not-intentionally added, being incorporated in the formed rare-earth doped alkaline-earth silicon nitride phosphor ($AE_2Si_5N_8$:RE). Such silicon nitride based phosphors form phosphors with Improved chemical composition and optical properties. Such rare-earth doped silicon nitride based materials strongly absorb UV-blue light and convert it efficiently into yellow-orange-red light, and therefore they can be used as a phosphor for light sources and displays, especially for Light Emitting Diodes (LED) and Scanning Beam Displays working with UV and purple laser as exciting source, as well as radiation converter in other devices. The invention further relates to a phosphor obtainable by such a method and to a radiation-emitting device comprising such a phosphor.

BACKGROUND OF THE INVENTION

[0002] A method of the kind mentioned in the opening paragraph is known from EP 1 104 799 A1. It is described how in this way e.g. Eu^{2+}-doped $M_2Si_5N_8$ (M = Ca, Sr, Ba) is manufactured that strongly absorbs UV-blue radiation and converts this absorbed radiation efficiently into red light.

[0003] A drawback of the known method is that the conversion efficiency of the phosphors obtained by said method is not satisfying. Moreover, the conversion efficiency drops due to degradation of the phosphor.

[0004] WO 2006/126567 A1 teaches nitride and oxynitride phosphors wherein an alkaline earth metal element is substituted by an element having a lower valance. Further, nitrogen ions can be substituted by oxygen ions. An embodiment of this phosphor is represented by the formula $Sr_2Al_qSi_{5-q}N_{8-q}O_q$:Eu.

[0005] In US 2007/0114548 A1, a phosphor of the general formula $Ca_{1-g-h-i}Ce_g(Li, Na)_hEu_iAl_{1+g-h}Si_{1-g+h}N_3$ is shown. The integration of monovalent ions Li^+, Na^+ is linked to the integration of Ce^{3+} ions that replace Ca^{2+} ions and/or to the integration of Si^{4+} ions that replace Al^{3+} ions.

[0006] WO 2005/083037 A1 teaches a phosphor of the general formula $(Sr_{1-x-y}Ba_xCa_y)_{2-a}Al_aN_{8-a}:Eu_z$.

[0007] WO 2004/055910 A1 teaches a phosphor of the general formula $(Sr_{1-x-y}Ba_xCa_y)_{2-z}Si_{5-a}Al_aN_{8-a}O_a:Eu_z$ wherein $0 < a < 5$.

OBJECT AND SUMMARY OF THE INVENTION

[0008] For that reason the present invention aims at providing a method of manufacturing providing a phosphor with still higher conversion efficiency and an excellent life-time.

[0009] According to the invention that aim is reached in a method according to claim 1.

[0010] The invention is based on the conclusion that unsatisfactory properties of the above-mentioned known phosphors result from the creation of defects by formation of a non stoichiometric oxygen containing phosphor. Besides the steps mentioned in the opening paragraphs the inventive method is characterized in that the creation of defects by formation of a non stoichiometric oxygen containing phosphor is at least partly prevented by partly substituting for the ions (AE, Si, N) of the alkaline-earth silicon nitride phosphor ($AE_2Si_5N_8$) suitable further elements of the periodic system by which vacancies are created, filled or annihilated resulting in the formation of a modified alkaline-earth silicon nitride phosphor ($AE_2Si_5N_8$) having a (more) stoichiometric composition. In this way a modified phosphor is obtained with excellent optical luminescence properties like the spectral distribution of the converted radiation but with in particular a very high conversion efficiency and very moderate degradation behavior.

[0011] The present invention is based on the following surprising recognitions. Firstly the inventor realized that small amounts of oxygen are intentionally or un-intentionally added in the starting materials or during the manufacturing process. An example of the first is the addition of small amounts of europium oxide (Eu_2O_3) to the compounds used for forming the phosphor. Although the firing of said compounds to obtain the phosphor normally is performed under a reducing ambient of e.g. a mixture of nitrogen and hydrogen, the inventor realized that not all the oxide thus added is removed. Moreover, un-intentional addition of oxygen can occur since the pure starting materials may contain oxide impurities that are not completely or even not at all removed during the manufacturing. An example of such an impurity is silicon dioxide (SiO_2) that may be present in various amounts in a starting material like silicon nitride (Si_3N_4). A second recognition is that the presence of oxygen may lead to formation of a non-stoichiometric compound on the phosphor crystal lattice of the nitrido silicate type comprising comer-sharing SiN4 tetraeders and having various crystal structures like the monoclinic or orthorhombic structures. This may be indicated by the following formula:

$$AE_2Si_5N_{8-x}O_{3/2*x}$$

[0012] This equation shows that if a fraction x of the nitrogen ions is replaced by oxygen ions, the resulting compound must contain 3/2*x Oxygen atoms in order to obtain charge-neutrality. Whereas only a fraction x is available for positioning O ions on N sites the retaining 1/2*x O atoms have to be positioned elsewhere. This may be e.g. in the form of an interstitial (1/2) oxygen atom. Such a defect will influence the conversion efficiency in negative manner and also may enhance degradation of the phosphor.

[0013] Creation of an anion vacancy in the phosphor crystal lattice can be used according to the invention to avoid the formation of such an interstitional oxygen defect in a manner that will be discussed below.

[0014] More likely however at least a part of the superfluous oxygen atoms are positioned on an N ion position in an additional unit cell. However, for reasons of charge neutrality this anion interstitial defect is equivalent to the creation of a cation vacancy on the cation sublattice that also has the above negative effects on the phosphor properties.

[0015] Furthermore, the invention is based on the recognition that by substituting suitable elements of the periodic system for the ions forming the (rare-earth doped) alkaline-earth silicon nitride phosphor, said defects can be avoided by creating, filling or annihilating vacancies. Moreover, with the method of the present invention also segregation of the phosphor into two or more compounds is substantially prevented. Such segregation also is detrimental for the conversion efficiency and the degradation behavior of the phosphor. Thus, with a method according to the invention a phosphor with a very high efficiency is obtained since the number of defects such as interstitials and vacancies that will act as centers for non-radiative recombination and the possibility of segregation is reduced. At the same time degradation behavior of the phosphor is improved.

[0016] The suitable elements form anions for replacement of nitrogen anions and having a larger negative charge than the nitrogen ions that they replace. In this way also anion vacancies are created that can annihilate the cation vacancies formed by excess oxygen on the nitrogen sublattice. Similarly, the formation of an interstitial oxygen defect will be avoided since the created anion vacancy can be occupied by an oxygen atom that otherwise could form an interstitial. This creation of an anion vacancy is formed by replacing a part of the nitrogen ions (N) by carbon ions (C).

[0017] Preferably the creation of vacancies is substantially completely prevented by the incorporation of appropriate amounts of the further elements in the phosphor. For this reason an advantageous modification is characterized in that in order to determine the suitable amount of further elements the oxygen content in the starting compounds and/or the amount of oxygen introduced during the reaction process are determined.

[0018] In a preferred modification, the amount of oxygen within the inventive phosphor can be minimized by obviating nitrates, carbonates, oxalates, acetates, or the like as starting materials. Only residual oxygen present e.g. in technically available nitrides will be present in the resulting phosphor.

[0019] In a further modification for the compounds solid compounds are chosen that are grinded and mixed and heated in a furnace under an ambient that is free or at least substantially free of oxygen. Apart from (substantially) oxygen free, such an ambient may be even reducing such as an ambient comprising a mixture of nitrogen and hydrogen. Although other manufacturing methods, like using the MOVPE or MOVPD (= Metal Organic Vapor Phase Epitaxy/Deposition) or the so-called Sol-Gel technique, the method of this solid-state synthesis embodiment implies several important advantages. The heating may be done e.g. in the temperature range of 1200 to 1700 degrees Celsius and preferably between 1300 and 1600 degrees Celsius for the above solid state synthesis method.

[0020] In a preferred modification for the compounds used in forming the phosphor only compounds are selected that do not contain intentionally added oxygen. In this way the oxygen compound in the modified phosphor is as low as possible. The modified phosphor compound in this case has a formula that is as close as possible to e.g. $AE_2Si_5N_8$:RE.

[0021] The invention further comprises a modified rare-earth doped alkaline-earth silicon nitride phosphor ($AE_2Si_5N_8$:RE) obtainable by a method according to the invention. The composition obeys $AE_2Si_5N_{8-2x}C_xO_x$:RE, wherein again x is smaller than 1, more preferably smaller than 0.25 and more preferably between 0 and 0.1. The symbols AE and RE have the same meaning as indicated before. It is to be noted that also phosphors can be obtained, which form a mixture of the above mixed crystals. Thus substitution may simultaneously occur at both the AE sublattice as on the silicon lattice as on the nitrogen sublattice.

[0022] In the case of substituting the nitrogen ions in the anionic sublattice by negative charged carbon ions another aspect should be regarded. Besides the effect of compensating vacancies the incorporation of carbon ions (C^{4-}) in the nitride anion sublattice can have further positive effects on the phosphor properties e.g. on phosphor stability against degradation. These further effects would be due to the stronger covalent Si-C bonding compared to the Si-N bonding. The incorporation of C in a nitride lattice and the formation of a Si-C bonding are already known for carbidonitridosilicate compounds like $Re_2Si_4N_6C$. Therefore, it can be favourable to add more SiC as it is necessary for the compensation of the determined and calculated oxygen amount. In that case further charge compensating elements like (1-) charged anions X (e.g. halogen ions like F^-), (3+) charged cations M (e.g. La^{3+}, Sc^{3+}, Y^{3+} or other (3+) charged rare-earth ions) and/or (5+) charged cations (e.g. P^{5+}, Ta^{5+}, V^{5+}) have to be incorporated by substitution of N^{3-} anions, alkaline-earth ions and silicon ions, respectively resulting in phosphor compositions which obey for example the formulas

$AE_2Si_5N_{8-2x-3z}O_xC_{x+2z}F_z$, or $Sr_{2-z}La_zSi_5N_{8-2x-z}O_xC_{x+z}$.

[0023] Finally the invention comprises a radiation converting device for the transformation of UV, purple and blue radiation into yellow-orange-red light containing a modified rare-earth doped alkaline-earth silicon nitride phosphor ($AE_2Si_5N_8$:RE) obtainable with a method according to the invention. For example, as relevant technical devices, fluorescent lamps, coloured light or white emitting LED's, special Scanning Beam Displays based on UV or purple laser excitation and also photovoltaic cells as well as greenhouse foils and glasses can be regarded. However, the invention is not limited to those examples.

[0024] It is to be noted here that the notation chosen to represent the rare-earth doping, i.e. "formula: RE", is chosen for reasons of simplicity and for expressing that the RE element forms a doping element and may be present in a relatively small quantity. However, in the present invention also oxygen and the suitable substitution elements are present in relatively low concentrations in the mixed crystal of the phosphor compound. Thus, also a representation by "formula" in which the RE element is represented and handled in the same manner as the other constituents (AE, Si, N, O) of the phosphor compound is feasible. In fact the RE element may be present also in high quantity relative to the AE element up to even a 100 percent replacement of the AE element by the RE element.

DESCRIPTION OF EMBODIMENTS

[0025] It is further to be noted that silicon nitride based materials can be prepared in different ways, e.g. solid state synthesis starting from the nitrides, nitridation of elemental starting materials or carbothermal reduction and nitridation of oxide starting materials. Ammonolysis of oxide based starting materials, comprising the heating in NH_3 containing atmosphere, is also a possible route. The solid-state synthesis method is normally used to prepare the $M_2Si_5N_8$:Eu phosphor material starting from (nitrided) Eu and M (alkaline earth) metals together with Si_3N_4.

[0026] For example, the preparation of Eu^{2+} doped $M_2Si_5N_8$ (M=Ba, Sr, Ca) can be as follows. The binary nitride precursors SrN_a ($a \approx 0.6$ - 0.66), BaN_b ($b \approx 0.6$ - 0.66) and EuN_c ($c \approx 0.94$) can be pre-prepared by the reaction of the pure strontium metal, barium metal and Eu metal under flowing dried nitrogen at 800, 550, and 800°C, respectively, for 8-16 hours. In addition, calcium nitride powder Ca_3N_2 and α -Si_3N_4 powder can be used as the as-received raw materials. Polycrystalline $M_{2-y}Eu_ySi_5N_8$ ($0\leq y\leq 0.2$ for M = Ca, $0\leq y\leq 2.0$ for M = Sr, Ba) powders can be prepared by a solid state reaction method at moderately high temperature. The Ca_3N_2,SrN_a, BaN_b and EuN_c as well as α -Si_3N_4 powders are weighed out in the appropriate amounts and subsequently mixed and ground together in an agate mortar. The powder mixtures are then transferred into e.g. molybdenum crucibles. All processes are carried out in a purified-nitrogen-filled glove-box. Subsequently those powder mixtures are fired twice (with a medium grinding in between) in a horizontal tube furnace at 1300 - 1400°C for 12 and 16 hours, respectively, under flowing 90% N_2-10% H_2 atmosphere.

[0027] A description is given for the solid-state synthesis route of silicon nitride based materials starting with Si_3N_4 as starting material. Different options to compensate the oxygen present in the starting material Si_3N_4 (that means that actually SiO_2 is present) for e.g. $Sr_2Si_5N_8$:Eu is:

[0028] With C^{4-} (e.g. by the addition of SiC)

[0029] Due to the replacement of a $(OC)^{6-}$ pair by an equally charged $(N_2)^{6-}$ pair, the overall stoichiometry of the host-lattice is maintained, and no defects (like vacancies or interstitials) are formed. This can be achieved by adding SiC to the reaction mixture in the amount required to consume the oxygen present in the starting Si_3N_4 material (as SiO_2) according to the reaction equation: $SiO_2 + 2\ SiC \rightarrow Si_3C_2O_2$, resulting in a compound with the same stoichiometry as the " ideal" Si_3N_4 material (without oxygen). An example of the resulting phosphor is $(Sr,Eu)_2Si_5N_{8-2x}O_xC_x$.

[0030] The proposed idea not only can be used for the compensation of oxygen present In Si_3N_4, but also in the starting materials containing Sr and Eu. The proposed idea makes it possible to use relatively small quantities of (cheaper and more convenient) oxide starting materials, like SrO ($SrCO_3$) and Eu_2O_3.

[0031] The synthesis conditions concerning mixing procedure, firing temperature and atmosphere as well as further properties, aspects, and advantages of the invention will be discussed in more detail below with reference to three examples with various oxygen contents. Starting materials are Si_3N_4 (either α or β), SrN_a (or nitrided Sr) and/or small quantities of SrO (or $SrCO_3$) and EuN_c (or nitrided Eu) and/or small quantities of Eu_2O_3, while AlN or SiC is added for charge compensating the residual amounts of oxygen (e.g. present in Si_3N_4) or the intentionally added amounts of oxygen (e.g. as SrO or Eu_2O_3).

Example 1:

[0032] 230 g α-Si_3N_4 (oxygen content 0.6 wt%), 3.64 g SiC, 6.08 g Eu (which is nitrided in N_2 atmosphere at 800°C) and 172 g Sr (which is nitrided in N_2 atmosphere at 800°C) are subsequently mixed under dry nitrogen atmosphere. That mixture is filled into thermal and chemical stable crucibles and fired in a N_2/H_2 atmosphere at 1350-1600°C for 8-24 h. The resulting phosphor can be represented by the following formula: $Sr_{2-y}Eu_ySi_5N_{8-2x}O_xC_x$ wherein x = 0.086 and y = 0.04.

Example 2:

[0033] A mixture of 218 g α -Si_3N_4 (oxygen content 1.0 wt. %), 15.05 g SiC, 26.39 g Eu_2O_3 and 162 g Sr (which is nitrided in N_2 atmosphere at 800°C)) is prepared and fired in the same way as it is described in example 1. The resulting phosphor can be represented by the following formula:
$Sr_{2-y}Eu_ySi_5N_{8-2x}O_xC_x$ wherein x = 0.361 and y= 0.15.

[0034] The invention was described above with reference to preferred embodiments thereof. Those skilled in the art will appreciate that numerous modifications may be applied thereto without departing from the scope of the accompanying claims. The description should accordingly be regarded as illustrative rather than restrictive, and no limitations are to be inferred other than those stated in the claims.

[0035] Although the invention is particularly suitable for a phosphor made by grinding and heating, it can be also applied in other manufacturing methods such as those mentioned above like MOVPE. In the method use can be made of fluxes or additives for influencing particle size and/or particle morphology.

[0036] Instead of doping with a single rare-earth ion, doping with more than one of such ions, e.g. Eu and Ce, may be considered. Also co-doping or co-activation with transition metal ions is feasible.

[0037] Further it is to be noted that in the examples Sr can be partly or completely be replaced by Mg or Ca or Ba or the like or by a combination of such elements. In this respect it is to be noted that the alkaline-earth elements may be partly replaced by other suitable metallic ions with a 2+ charge like in particular Zn-ion.

[0038] Although the invention in particular aims at the manufacture of a modified alkaline-earth silicon nitride phosphor with a composition close to $AE_2Si_5N_8$:RE it may equally well be applied to the preparation of other modified alkaline-earth silicon nitride phosphor compounds with a composition close to other known compounds of the elements AE, Si and N. Examples of the latter are $AESi_7N_{10}$ or $AESiN_2$. The invention equally deals with the corresponding obtainable phosphor compounds in which suitable substitutions are performed and with a radiation converting device comprising the latter.

[0039] Other excitation methods may be used than the one mentioned, e.g. Cathode-ray or X-ray excitation, electro-luminescence etc. Other forms than powders may be used for the compound used in the method according the invention e.g. monocrystals, thin films, ceramics (a sintered powder), and co-coating in which the compound is formed on a nucleus of another material or in which the compound is coated by another material.

[0040] Finally it is also to be noted that although the method according to the invention preferably implies the formation of the desired phosphor compound using a synthesis based on two or more compounds, it also comprises the method in which one compound that has been already made according to the composition of a desired phosphor is treated with a (or several) further compound in order to remove defects and/or segregation in the phosphor by forming a modified compound in which defects are removed by creating, filling or annihilating vacancies.

Claims

1. A method of manufacturing a rare-earth doped alkaline-earth silicon nitride phosphor, said method comprising the steps of:

   - selecting one or more compounds each comprising at least one element of the group comprising the rare-earths elements, the alkaline-earth elements, silicon and nitrogen and together comprising the necessary elements to form the rare-earth doped alkaline-earth silicon nitride phosphor;
   - bringing the compounds at an elevated temperature in the range between 1,200 and 1,700 degrees Celsius in reaction for forming the rare-earth doped alkaline-earth silicon nitride phosphor, whereby an amount of oxygen is being incorporated in the rare-earth doped alkaline-earth silicon nitride phosphor thus formed, **characterized in that**
   - partly substituting nitrogen anions of the alkaline-earth silicon nitride phosphor for carbon by which vacancies are created, filled or annihilated within the lattice of the phosphor resulting in the formation of a modified alkaline-earth silicon nitride phosphor having a stoichiometric composition as to at least partly prevent the creation of defects by formation of a non stoichiometric oxygen containing alkaline-earth silicon nitride phosphor, wherein the resulting rare-earth doped alkaline-earth silicon nitride phosphor is **characterized by** a general formula of:
   $AE_2Si_5N_{8-2x}C_xO_x$:RE
   wherein AE is an alkaline-earth element;
   RE is a rare earth element;
   and wherein x is smaller than 1

2. Method according to claim 1, **characterized in that** the creation of defects is substantially completely prevented by the incorporation of suitable amounts of carbon in the phosphor.

3. Method according to claim 2, **characterized in that** in order to determine the suitable amount of carbon the oxygen content in the starting compounds and/or the amount of oxygen introduced during the reaction process are determined.

4. Method according to anyone of the preceding claims, **characterized in that** for the compounds solid com-

pounds are chosen that are grinded and mixed and heated in a furnace under a reducing ambient.

5. A modified rare-earth doped alkaline-earth silicon nitride phosphor obtainable by a method according to any of the preceding claims.

6. A modified rare-earth doped alkaline-earth silicon nitride phosphor as claimed in claim 5 **characterized in that** x is smaller than 0.25 and more preferably smaller than 0.1.

7. A radiation emitting device comprising a modified rare-earth doped alkaline-earth silicon nitride phosphor as claimed in claims 5 or 6.

8. A radiation converting device comprising a modified rare-earth doped alkaline-earth silicon nitride phosphor as claimed in claim 5 or 6.

Patentansprüche

1. Verfahren zur Herstellung eines seltenerddotierten Erdalkalisiliciumnitrid-Leuchtstoffs, wobei das Verfahren folgende Schritte umfasst:

- Auswählen einer oder mehrerer Verbindungen, welche jeweils mindestens ein Element aus der die Seltenerdelemente, die Erdalkalielemente, Silicium und Stickstoff umfassenden Gruppe umfassen, und welche zusammen die erforderlichen Elemente umfassen, um den seltenerddotierten Erdalkalisiliciumnitrid-Leuchtstoff zu bilden;
- Zur-Reaktion-Bringen der Verbindungen bei einer erhöhten Temperatur im Bereich zwischen 1.200°C und 1.700°C, um den seltenerddotierten Erdalkalisiliciumnitrid-Leuchtstoff zu bilden, wobei in den so gebildeten seltenerddotierten Erdalkalisiliciumnitrid-Leuchtstoff eine Menge an Sauerstoff eingebaut wird,

dadurch gekennzeichnet, dass

- partielles Ersetzen der Stickstoff-Anionen des Erdalkalisiliciumnitrid-Leuchtstoffs durch Kohlenstoff, wodurch innerhalb des Leuchtstoffgitters Fehlstellen erzeugt, gefüllt oder beseitigt werden, was zu der Bildung eines modifizierten Erdalkalisiliciumnitrid-Leuchtstoffs führt, der eine stöchiometrische Zusammensetzung aufweist, um die Erzeugung von Defekten durch Bildung eines nicht stöchiometrischen sauerstoffhaltigen Erdalkalisiliciumnitrid-Leuchtstoffs zumindest teilweise zu verhindern, wobei der resultierende seltenerddotierte Erdalkalisiliciumnitrid-Leuchtstoff durch die folgende allgemeine Formel gekennzeichnet ist:

$AE_2Si_5N_{8-2x}C_xO_x$:RE,

wobei

- AE für ein Erdalkalielement steht;
- RE für ein Seltenerdelement steht;

und wobei x kleiner als 1 ist.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** die Erzeugung von Defekten durch den Einbau geeigneter Mengen an Kohlenstoff in den Leuchtstoff weitgehend vollständig verhindert wird.

3. Verfahren nach Anspruch 2, **dadurch gekennzeichnet, dass** der Sauerstoffgehalt in den Ausgangsverbindungen und/oder die Menge des während des Reaktionsprozesses eingeführten Sauerstoffs ermittelt wird, um die geeignete Menge an Kohlenstoff zu ermitteln.

4. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die Verbindungen als feste Verbindungen ausgewählt werden, welche zerkleinert und vermischt und in einer reduzierenden Umgebung in einem Ofen erwärmt werden.

5. Modifizierter seltenerddotierter Erdalkalisiliciumnitrid-Leuchtstoff, welcher durch ein Verfahren nach einem der vorhergehenden Ansprüche zu erhalten ist.

6. Modifizierter seltenerddotierter Erdalkalisiliciumnitrid-Leuchtstoff nach Anspruch 5, **dadurch gekennzeichnet, dass** x kleiner als 0,25; vorzugsweise kleiner als 0,1 ist.

7. Strahlungsemittierende Vorrichtung, welche einen modifizierten seltenerddotierten Erdalkalisiliciumnitrid-Leuchtstoff nach Anspruch 5 oder 6 umfasst.

8. Stahlungskonvertierende Vorrichtung, welche einen modifizierten seltenerddotierten Erdalkalisiliciumnitrid-Leuchtstoff nach Anspruch 5 oder 6 umfasst.

Revendications

1. Procédé de fabrication d'un phosphore de nitrure de silicium alcalino-terreux dopé aux terres rares, ledit procédé comprenant les étapes consistant à :

- choisir un ou plusieurs composés comprenant chacun au moins un élément du groupe comprenant les éléments de terres rares, les éléments alcalino-terreux, le silicium et l'azote et comprenant ensemble les éléments nécessaires à la formation de phosphore de nitrure de silicium alcalino-terreux dopé aux terres rares ;

- porter les composés à une température élevée dans la plage de 1 200 à 1 700°C dans une réaction de formation de phosphore de nitrure de silicium alcalino-terreux dopé aux terres rares, une quantité d'oxygène étant ainsi incorporée dans le phosphore de nitrure de silicium alcalino-terreux dopé aux terres rares ainsi formé,

caractérisé en ce que

- la substitution partielle des anions azote du phosphore de nitrure de silicium alcalino-terreux à du carbone entraîne la création, le remplissage ou l'annihilation de trous dans la matrice du phosphore résultant en la formation d'un phosphore de nitrure de silicium alcalino-terreux modifié ayant une composition stoechiométrique de manière à au moins partiellement prévenir la création de défauts par formation d'un phosphore de nitrure de silicium alcalino-terreux contenant de l'oxygène non stoechiométrique, le phosphore de nitrure de silicium alcalino-terreux dopé aux terres rares obtenu étant **caractérisé par** une formule générale :

$AE_2Si_5N_{8-2x}C_xO_x$: RE
dans laquelle
AE est un élément alcalino-terreux ;
RE est un élément de terres rares ;
et dans laquelle x est inférieur à 1.

2. Procédé selon la revendication 1, **caractérisé en ce que** la création de défauts est sensiblement totalement empêchée par l'incorporation de quantités adaptées de carbone dans le phosphore.

3. Procédé selon la revendication 2, **caractérisé en ce que** de manière à déterminer la quantité adaptée de carbone, la teneur en oxygène dans les composés de départ et/ou la quantité d'oxygène introduite durant le procédé de réaction sont déterminées.

4. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** pour les composés, des composés solides sont choisis qui sont broyés puis mélangés et chauffés dans un fourneau sous une atmosphère réductrice.

5. Phosphore de nitrure de silicium alcalino-terreux dopé aux terres rares modifié pouvant être obtenu par un procédé selon l'une quelconque des revendications précédentes.

6. Phosphore de nitrure de silicium alcalino-terreux dopé aux terres rares modifié selon la revendication 5, **caractérisé en ce que** x est inférieur à 0,25 et de préférence inférieur à 0,1.

7. Dispositif émetteur de rayonnement qui comprend un phosphore de nitrure de silicium alcalino-terreux dopé aux terres rares modifié selon les revendications 5 ou 6.

8. Dispositif convertisseur de rayonnement qui comprend un phosphore de nitrure de silicium alcalino-terreux dopé aux terres rares modifié selon la revendication 5 ou 6.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- EP 1104799 A1 **[0002]**
- WO 2006126567 A1 **[0004]**
- US 20070114548 A1 **[0005]**
- WO 2005083037 A1 **[0006]**
- WO 2004055910 A1 **[0007]**