

Ce³⁺, Eu²⁺ and Mn²⁺-activated alkaline earth silicon nitride phosphors and white-light emitting LED

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(54) Title: CE3+, EU2+ AND MN2+ - ACTIVATED ALKALINE EARTH SILICON NITRIDE PHOSPHORS AND WHITE-LIGHT EMITTING LED

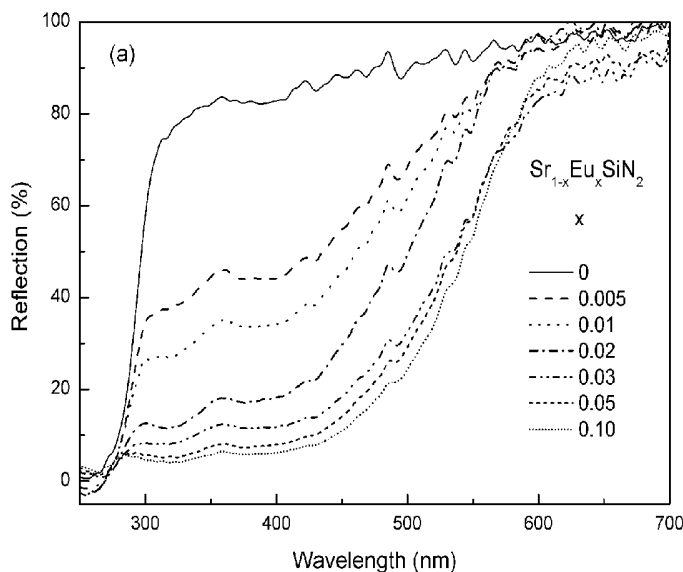


Fig. 1 (a)

(57) Abstract: The invention refers to an alkaline earth silicon nitride phosphor of the MSiN₂ type that is activated by Ce³⁺ and/or Eu²⁺ and/or Mn²⁺ ions. A preferred embodiment of the phosphor is defined by the general formula MSiN₂:A, wherein M is a divalent metal ion, especially Mg, Ca, Sr, Ba, Be and/or Zn, and A is an activator chosen from the group Ce³⁺, Eu²⁺ and/or Mn²⁺. A preferred application for this phosphors is a white-light emitting LED using the phosphor for conversion of radiation.

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**Ce³⁺, Eu²⁺ and Mn²⁺ - activated Alkaline Earth Silicon Nitride
Phosphors and white-light emitting LED**

The invention refers in general to efficient anorganic nitride
5 phosphors which can applied in various technical applications
such as fluorescent lamps, coloured light or white emitting
LEDs, special scanning beam displays working with UV or purple
laser as exciting source, and other devices where phosphors are
used to convert especially UV radiation or blue light into
10 visible and/or IR radiation.

In the last few years some new nitride and oxynitride phosphors
have been developed for the above mentioned applications.
Nitridosilicates, oxynitridosilicates, or oxynitridoaluminosilicates
15 activated by rare earth ions, such as $M_2Si_5N_8: Eu^{2+}$,
 Ce^{3+} , $MSi_2O_{2-8}N_{2+2/38}: Eu^{2+}$, Ce^{3+} (M=Ca, Sr, Ba), $MYSi_4N_7$ (M = Sr, Ba):
 Eu^{2+} , Ce^{3+} , $MSi_xAl_{2-x}O_{4-x}N_x: Eu^{2+}$ (M=Ca, Sr, Ba), α -SiAlON: RE (RE
= Eu^{2+} , Ce^{3+} , Yb^{2+} , Tb^{3+} , Pr^{3+} , Sm^{3+}), β -SiAlON: Eu^{2+} , and
 $CaAlSiN_3:Eu^{2+}$ emit visible light efficiently under near-ultra-
20 violet or blue light irradiation and have improved thermal and
chemical stabilities compared to their oxide and sulfide
counterparts, allowing them to be used as high performance
down-conversion luminescent materials for white light-emitting
diodes (LEDs) applications for example.

25 Recently, a series of other nitridosilicate compounds with the
general chemical formula $MSiN_2$ (M = Mg, Ca, Sr, Ba) was
presented as suitable host lattices for Eu^{2+} or Ce^{3+} -activated
phosphors. First, the photoluminescence properties of
30 $MgSiN_2:Eu^{2+}$ after excitation with UV radiation were described by
G.K. Gaido et al. (Izv. Akad. Nauk SSSR. Neorg. Mater. 10
(1974) page 564-566). Somewhat later $CaSiN_2$ was investigated as
new phosphor in electroluminescence device applications by
S.S.L. Lee et al. (SPIE Proceedings 3241 (1997), p. 77) and

additionally, $\text{SrSiN}_2:\text{Eu}^{2+}$ and $\text{BaSiN}_2:\text{Eu}^{2+}$ phosphors have been proposed as suitable red and green emitting conversion materials in WO 2005/103199 A.

5 In a more recent publication Le Toquin and A.K. Cheetham (Chem. Phys. Lett. 423 (2006) pages 352-356) reported, however, about Ce^{3+} -activated CaSiN_2 as a red emitting phosphor which can be used especially in order to increase CRI values in warm-white LEDs.

10

The advantages of these types of phosphors should be in an efficient emission of visible light, mainly at longer wavelengths, after excitation with near-ultraviolet or blue light due to high covalency and strong crystal field in this kind of nitride host lattices. This could make it interesting for application in white-emitting LEDs.

15

Furthermore, contrary to other highly condensed nitridic phosphors, which requires very high temperature for their synthesis, the phosphors based on MSiN_2 host lattices may be prepared at clearly reduced temperatures. Thus production costs can be reduced.

20

However, compared with other nitrides as for example $\text{M}_2\text{Si}_5\text{N}_8$ or $\text{MSi}_7\text{N}_{10}$ which are characterized by strong inorganic networks the MSiN matrix and the related phosphors show a higher tendency to chemical degradations especially under harmful environmental conditions like moisture or reactive gases, unfortunately.

25

30

Therefore an object of the present invention is to provide improved and modified rare earth and/or manganese activated MSiN_2 type phosphors which are more stabilized against chemical degradations in general. For this reason it is an important

object of the invention to indicate a method for stabilizing the MSiN_2 phosphors and to protect them against harmful environmental conditions like moisture, reactive gases or chemicals. A further object of the invention is to provide a white-light emitting LED which is more stabilized against chemical degradations.

The named object is achieved by a phosphor according to accompanying claim 1 and by a LED according to accompanying claim 11.

The present invention discloses improved, modified and specially stabilized alkaline earth silicon nitride phosphors of the MSiN_2 type that are activated by Ce^{3+} - and/or Eu^{2+} - and/or Mn^{2+} - Ions.

In a preferred embodiment of the invention, the stabilized phosphor have the general formula $\text{MSiN}_2:\text{A}$, wherein M is a divalent metal ion like Mg, Ca, Sr, Ba, Be and/or Zn and A is an activator chosen from the group Ce^{3+} , Eu^{2+} and/or Mn^{2+} .

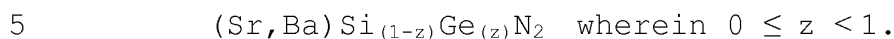
In a further preferred embodiment of the invention, the stabilized MSiN_2 phosphor can be described by one of the following formulas: $\text{SrSiN}_2:\text{Eu}^{2+}$, $\text{BaSiN}_2:\text{Eu}^{2+}$, $\text{SrSiN}_2:\text{Ce}^{3+}$, $\text{BaSiN}_2:\text{Ce}^{3+}$, $\text{SrSiN}_2:\text{Mn}^{2+}$ and $\text{BaSiN}_2:\text{Mn}^{2+}$.

It is a special embodiment of the invention that the SrSiN_2 and BaSiN_2 lattices can be mixed to $\text{Sr}_{(1-x)}\text{Ba}_x\text{SiN}_2$ solid solutions, wherein $0 \leq x \leq 1$.

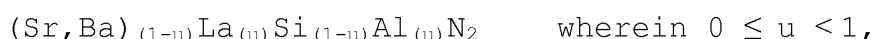
In further embodiments of the invention, Sr-ions and/or Ba-ions may be replaced partially or completely by other divalent metal ions M like Mg, Ca, Zn, Be resulting in the following formula of the host lattice:



On the other side Si can be replaced partially by Ge resulting in the formula:

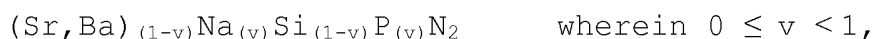


Further possibilities of substitutions concern the replacement of $[(\text{Sr}, \text{Ba})\text{Si}]^{6+}$ by $(\text{LaAl})^{6+}$ resulting in:



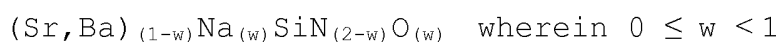
10 whereby La can also be replaced partially or completely by Sc, Y, and/or another rare earth element and Al can be substituted partially or completely by B, Ga, and/or Sc.

Likewise $[(\text{Sr}, \text{Ba})\text{Si}]^{6+}$ can be partially replaced by the $(\text{NaP})^{6+}$ group accordingly:

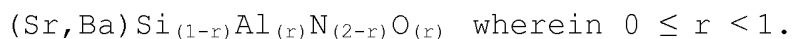


whereby in place of Na also Li, K, Rb, and/or Cs can be incorporated partially or completely into the phosphor matrix.

20 In a further embodiment of the invention, $[(\text{Sr}, \text{Ba})\text{N}]^-$ is replaced partially by $(\text{NaO})^-$ resulting in the formula:



25 whereby Na can be replaced partially or completely by Li, K, Rb, and/or Cs; and $(\text{SiN})^+$ can be partially substituted by a $(\text{AlO})^+$ structural unit which leads to the formula:



In the last case Al can be also replaced partially or completely by B, Ga, and/or Sc.

30 All these substitutions of the improved, modified and stabilized phosphors according to the invention can be made, in order to realize a fine tuning of the luminescence characteristics of the phosphors. In this way the phosphor characteristics

can be adapted optimally to the requirements of technical application.

5 In all cases the respective host lattices of the phosphor compositions are activated with Ce^{3+} - and/or Eu^{2+} - and/or Mn^{2+} ions. The activator concentrations cover the range from nearly zero up to 0.5 atomic portions, or from nearly zero up to 50 atomic per cent.

10 It is a further embodiment of the invention, that also other rare earth ions like Ce, Yb, Tb, Gd, Dy, Sm or others may be incorporated into the phosphor lattice in order to act also as an activator, a co-activator and/or sensitizer of the activator luminescence. Particularly in case of the inventive Mn^{2+} -acti-
15 vated phosphors the introduction of sensitizer ions can leads to a remarkable improvement of the luminescence yield in particular for such exciting radiation, which can be absorbed neither by the host lattice nor by the Mn^{2+} -centers effectively.

20 Beside the rare earth ions also further ions like Pb^{2+} , Sn^{2+} , Cu^{2+}/Cu^+ , Sb^{3+} and Bi^{3+} can fulfil the function of an effective sensitizer for the Mn luminescence.

25 The concentrations of the co-activators and/or sensitizers are likewise accurately specified. They are adjusted in a range from larger/directly zero up to 50 atomic per cent.

30 It is a special advantage of the phosphors of the invention, that they possess a special chemical resistance against harmful environmental conditions. The improvement of chemical stability is realized by surface layers protect the phosphor from environmental conditions like moisture, reactive gases, e.g.

oxygen, and other reactive chemicals which cause chemical degradation of the phosphor properties.

5 The protective surface layers can be formed by surface coating or particle encapsulation with relevant organic or inorganic compounds. As coating for example fluorides, phosphates, oxides or nitrides of the elements Al, Si, Ti, Y, La, Gd or Lu or the alkaline-earth metals Mg, Ca, Sr or Ba can be used. The most important criteria for the choice for the coating materials
10 consist of that, that they offer an effective protection against environmental influences and that they exhibit optical windows both for the excitation and for the emission radiation in the situation of the technical applications of the phosphors of the invention.

15 In a preferred embodiment the surface of the phosphor is coated with fluoride compounds, especially with alkaline-earth metal fluorides. This kind of coating can be realized by chemical surface reactions of the host lattice compound with suitable
20 reactants like NH_4F , HF or mixtures of them.

The coating or encapsulation can also be achieved with the help of chemical vapor deposition (CVD) or plasma enhanced CVD (PECVD) or other coating technologies.

25 The inventive phosphors are preferably produced by a solid state reaction method at high temperature. As starting materials $\alpha\text{-Si}_3\text{N}_4$ and the nitrides of alkaline metals (e.g. Li_3N), alkaline-earth metals (Mg_3N_2 , Ca_3N_2 , SrN_x and/or BaN_x with $x=0\text{-}$
30 0.66), transition metals like Mn_3N_2 and/or rare earth metals (e.g. EuN_x , CeN) can be used. Afterwards, appropriate amounts of alkaline-earth nitrides, transition metals nitrides and/or rare earth metals nitrides as well as $\alpha\text{-Si}_3\text{N}_4$ powders are weighed out and subsequently mixed with a suitable common

mixing method. All those processes should be carried out in a purified-nitrogen-filled glove-box due to the sensitivity of some starting materials to air and humidity.

The powder mixtures transferred into suitable crucibles are
5 fired in high temperature furnaces at 1000-1400°C for 2-24 h under inert or reducing atmosphere. After firing, the samples were gradually cooled down to the room temperature in the furnace. Additionally, a suitable after-treatment of the phosphor material can be made.

10

The preparation method is not limited to the description above.

The phosphors of the invention may be also synthesised by methods starting with a mixture of Si_3N_4 and pure metals, which
15 are *in situ* nitrided. Furthermore, a mixture of Si_3N_4 , metal nitrides and pure metals can be used to prepare the phosphor. Also, mixtures of Si/Eu/Sr may be nitrided. Further, mixtures of C or C-containing substances like SiC as well as SiO_2 and the oxides of alkaline metals, alkaline-earth metals, transi-
20 tion metals and/or rare earth metals may be carbothermally reduced and nitrided. An ammonolysis of SiO_2 /metal oxides mixtures may be performed in NH_3 gas atmosphere. Metal oxide precursors like carbonates, sulfates and/or nitrates may also
25 be used instead of the oxides. Furthermore, CVD reactions between alkaline-earth metal/rare earth and/or transition metal/Si-precursors and NH_3 may be performed. Fluxes may be used in order to control particle shape and particle size distribution.

30

In the following the synthesis conditions are still described in more detail on the basis of 3 examples.

Example 1

0.005 mol of coated $\text{BaSiN}_2:\text{Eu}^{2+}$ (2 mol%) were produced by the method described below:

The binary nitride precursors BaN_x ($x \approx 0-0.66$) and EuN_x ($x \approx 0-1.0$)
5 were pre-prepared by the reaction of the pure barium metal (Aldrich, 99.9 %, pieces) and Eu metal (Csre, 99.9 %, lumps) under flowing dried nitrogen at 550 and 800 °C, respectively, for 12 h in a horizontal tube furnace. Afterwards, 0.7164 g $\text{BaN}_{0.633}$, 0.0165 g $\text{EuN}_{0.94}$ and 0.2339 g $\alpha\text{-Si}_3\text{N}_4$ powder (Permascand,
10 P95H, α content 93.2 % ; Oxygen content: ~1.5), were weighed out and subsequently mixed and ground together in an agate mortar. The powder mixtures were then transferred into molybdenum crucibles. All processes were carried out in a purified-nitrogen-filled glove-box. Subsequently, the powder mixtures
15 was fired in a horizontal tube furnace at 1250 °C for 16 h under flowing 90 % N_2 -10 % H_2 atmosphere. After firing, the sample was gradually cooled down to the room temperature in the furnace.

20 The protection layer of the inventive phosphor was formed by mixing one part of the prepared $\text{BaSiN}_2:\text{Eu}$ with 0.5 parts of a $\text{NH}_4\text{F}\cdot\text{HF}$ mixture after temperature treatment at 700°C for 5h in an inert atmosphere.

Example 2

Representative for Ce-doped MSiN_2 (M= Ba, Sr, Ca) phosphors
0,1 mol $\text{SrSiN}_2:\text{Ce}^{3+},\text{Li}^+$ (2 mol%) were prepared by the following way: The binary nitride precursor SrN_x ($x \approx 0-0.66$) was pre-prepared by the reaction of the pure strontium metal (Aldrich,
30 99.9 %, pieces), under flowing dried nitrogen at 800 °C for 12 h in a horizontal tube furnace. In addition, $\alpha\text{-Si}_3\text{N}_4$ powder (Permascand, P95H, α content 93.2 % ; Oxygen content: ~1.5), Ce (Alfa, >99 %, lumps) and Li (Merck, >99 %, lumps) are used as the as-received raw materials.

0,280 g Ce metal, 0,014 g Li metal, 9,089 g $\text{SrN}_{0,5036}$ as well as 4,676 g $\alpha\text{-Si}_3\text{N}_4$ powders were weighed out and subsequently mixed and ground together in an agate mortar. The powder mixtures
5 were then transferred into molybdenum crucibles. All the processes were carried out in a purified-nitrogen-filled glove-box. Subsequently the powder mixtures were fired in a horizontal tube furnace at 1250 °C for 16 h under flowing 90 % N_2 -10 % H_2 atmosphere. After firing, the samples were gradually cooled
10 down to the room temperature in the furnace.

Example 3

As an example for Mn^{2+} -activated MSiN_2 phosphors 0,01 mol of $\text{MgSiN}_2:\text{Mn}^{2+}$ (2 mol%) were synthesized as follows:
15 The 0,0110 g of Mn (Alfa, >99%), 0,3297 g Mg_3N_2 (Alfa, >98%) and 0,4676 g of $\alpha\text{-Si}_3\text{N}_4$ (Permascand, P95H, α content 93.2 % ; Oxygen content: ~1.5) powders were weighed out and subsequently mixed and ground together in an agate mortar. The powder
20 mixtures were then transferred into molybdenum crucibles. All those processes were carried out in a purified-nitrogen-filled glove-box. Subsequently, the powder mixtures were fired in a horizontal tube furnace at 1300 °C for 16 h under flowing 90 % N_2 -10 % H_2 atmosphere. After firing, the samples were gradually cooled down to the room temperature in the furnace.

25 The improved, modified and stabilized Eu^{2+} -, Ce^{3+} -, or Mn^{2+} -activated MSiN_2 type phosphors of the present invention show an effective luminescence in the range between 500 and 700 nm, whereby some of the inventive phosphors also emit also in the
30 IR region. Absorption bands arise within the range between 200 and 480 nm, so that the luminescence of the phosphors can be well excited using UV or blue light irradiation.

Due to the described luminescence characteristics the phosphor according to the present invention can be used as a radiation converter for the transformation of UV, purple or blue radiation into a longer-wave visible light that will be emitted by the phosphor preferably in green to red spectral region, and or IR radiation.

As appropriate technical devices fluorescent lamps, colored light or white emitting LED's, special scanning beam displays based on UV or purple laser excitation, and also for example photovoltaic cells or greenhouse foils or glasses can be regarded.

As excitation sources for the inventive phosphors high or low-pressure discharge plasmas, UV or blue emitting organic or inorganic light emitting diodes (LED) or appropriate lasers or laser diodes can be used.

The phosphors of the invention can be applied as single components in a relevant light emitting element or in combination with other red yellow, green, and/or blue-emitting phosphors in order to improve the performance of the respective application. The latter meets for example the improvement of the color rendering indices (CRI) of fluorescent lamps and white emitting LED's.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other features and advantages of the present invention will become more readily appreciated as the same become better understood by reference to the following detailed description of a preferred embodiment of the invention when taken in conjunction with the accompanying drawings, wherein:

- Fig. 1 Diffuse reflection spectra of $M_{1-x}Eu_xSiN_2$
(a) M=Sr, (b) M =Ba
- 5 Fig. 2 Diffuse reflection spectra of $M_{0.96}Ce_{0.02}Li_{0.02}SiN_2$
(M= Sr, Ba)
- Fig. 3 Emission spectra of $M_{1-x}Eu_xSiN_2$ under 400 nm excitation
(a) M=Sr, (b) M =Ba
- 10 Fig. 4 Excitation spectra of $M_{1-x}Eu_xSiN_2$
(a) M=Sr, (b) M =Ba
- Fig. 5 Typical excitation and emission spectra of
15 $SrSiN_2: Ce, Li$
- Fig. 6 Typical excitation and emission spectra of
 $BaSiN_2: Ce, Li$
- 20 Fig. 7 Emission spectra of $Mg_{1-x}Mn_xSiN_2$ under 254 nm
excitation
- Fig. 8 Excitation spectra of $Mg_{1-x}Mn_xSiN_2$
- 25 Fig. 9 The relative emission intensities of coated and
uncoated $M_{1-x}Eu_xSiN_2$ under 400 nm excitation for a
period of time.

All measurements were performed on finely ground samples, which
30 were analyzed by X-ray powder diffraction. All the samples are
shown to be pure phases and the powder X-ray diffraction
patterns of undoped or doped $MgSiN_2$, $SrSiN_2$ and $BaSiN_2$ samples
are in good agreement with the reported powders patterns in
JCPDS 52-0797, 22-1438 and 36-1257, respectively.

DETAILED DESCRIPTION

5 Fig. 1 shows the diffuse reflection spectra of undoped and
Eu²⁺-doped MSiN₂ (M = Sr, Ba) samples. Both undoped and Eu²⁺-
doped samples show a remarkable drop in reflection in the UV
range around 300 nm with an estimated band gap at about 258 nm
(≈ 4.8 eV) for M = Sr, 266 nm (4.7 eV) for M = Ba, corresponding
10 to the valence-to-conduction band transitions of the MSiN₂ host
lattice. The intense reflection in the visible spectral range
is in agreement with the observed grey-white body color for
undoped MSiN₂. Obviously, two broad absorption bands can be seen
from the reflection spectra of low Eu concentration samples.
15 One is the main absorption in the wavelength range of 350-
490 nm, another is a short-wavelength absorption band in the
wavelength range of 300-360 nm. The two broad absorption bands
both can be attributed to the absorption of the Eu²⁺ ions due to
the absence of them in undoped MSiN₂ samples. Moreover, the
20 intensities of them increase for higher Eu concentration. In
contrast to the undoped samples, the body color of M_{1-x}Eu_xSiN₂
shows light orange to orange for M = Sr and yellow to orange
for M = Ba varying with the Eu concentration ($0 < x \leq 0.1$) as a
result of a strong absorption in the visible range around 350 -
25 490 nm. Additionally, the onset of the reflection drop signifi-
cantly shifts to a longer-wavelength as the Eu concentration
increases indicating that the absorption range can be tailored
by the Eu content.

30 Fig. 2 shows the typical diffuse reflection spectra of Ce³⁺ and
Li⁺-codoped MSiN₂ (M=Sr, Ba). The diffuse reflection spectra of
undoped samples were also plotted as a comparison. Similarly
as it has been shown in the Fig. 1(a) and (b), there is a
remarkable drop in reflection in the UV range around 300 nm due

to the valence-to-conduction band transitions of the MSiN_2 host lattice. The intense reflection in the visible spectral range is in agreement with the observed grey-white body color for Ce^{3+} -doped MSiN_2 . Furthermore, the Ce^{3+} ion shows absorption in the UV-blue range (around 400 nm) in both SrSiN_2 and BaSiN_2 hosts.

Fig. 3 (a) and (b) show the typical emission spectra of $\text{Sr}_{1-x}\text{Eu}_x\text{SiN}_2$ and $\text{Ba}_{1-x}\text{Eu}_x\text{SiN}_2$ ($0 < x \leq 0.1$), respectively. Eu is present as the divalent ion in both Eu-doped BaSiN_2 and SrSiN_2 samples. $\text{Sr}_{1-x}\text{Eu}_x\text{SiN}_2$ ($0 < x \leq 0.1$) shows a broad emission band in the wavelength range of 550-850 nm with maxima from 670 to 685 nm with increasing the Eu concentration, while the sample of $\text{Ba}_{1-x}\text{Eu}_x\text{SiN}_2$ ($0 < x \leq 0.1$) shows a broad emission band in the wavelength range of 500-750 nm with maxima from 602 to 628 nm with the increasing the Eu concentration.

Typical excitation spectra of $\text{MSiN}_2:\text{Eu}^{2+}$ ($M = \text{Sr}, \text{Ba}$) are presented in Fig. 4. There are four dominated broad bands in the excitation spectra of $\text{MSiN}_2:\text{Eu}^{2+}$ ($M = \text{Sr}, \text{Ba}$). The position of these excitation bands is almost independent of the type of the M ions, the Eu concentration and the crystal structure, peaking at about 303, 340, 395 and 466 nm. Several weak excitation bands below 275 nm are readily assigned to the host lattice excitation (e.g. transition from the valence to conduction band for the MSiN_2 host lattices). The appearance of the excitation band of the host lattice in the excitation spectrum of Eu^{2+} indicates that there exists energy transfer from host lattice to Eu^{2+} ions. The remaining excitation bands in the wavelength range of 300-550 nm clearly originate from the transitions of Eu^{2+} , whereas the most intense excitation band of Eu^{2+} is located at about 395 nm in $\text{MSiN}_2:\text{Eu}^{2+}$. This excitation band of the Eu^{2+} ions is attributed to the influence of highly

covalent bonding of $M_{Eu}-N$ and a large crystal-field splitting due to the presence of nitrogen.

Since $MSiN_2:Eu^{2+}$ ($M = Sr, Ba$) materials have as well high
 5 absorption as efficient excitation in the spectral region of
 300- 490 nm, perfectly matching with the radiative light from
 the InGaN or GaN-based LEDs, these phosphors have a high poten-
 tial for using in white LED applications.

10 Table 1 summaries the composition, phase characteristics and
 luminescence properties of Eu^{2+} -doped $MSiN_2$ ($M=Mg, Ca, Sr, Ba$)
 for a comparison.

Table 1: Composition, phase characteristics and photolumines-
 15 cence properties of Eu^{2+} -doped $MSiN_2$
 ($M=Mg, Ca, Sr, Ba$) at room temperature

$M_{1-x}Eu_xSiN_2$	M=Mg $0 < x \leq 0.15$	M=Ca	M=Sr $0 < x \leq 0.1$	M=Ba $0 < x \leq 0.1$
Phase	MgSiN ₂	CaSiN ₂	SrSiN ₂	BaSiN ₂
Body color	-	-	Light orange to orange	Yellow to orange
Crystal system	Pna2 ₁	F 4b3m	P2 ₁ /c	Cmca
Host lattice band gap (eV)	4.8	4.5	4.8	4.7
Absorption bands of Eu^{2+} (nm)	275-410	-	300-490	300-490
Eu 5d excitation bands (nm)	277, 293, 316, 340, 375	-	303, 340, 395, 466	303, 340, 395, 466
Emission band maximum (nm)	517	620	670-685	602-628

Fig. 5 shows the typical excitation and emission spectra of SrSiN₂: Ce, Li. The sample displays a broad emission band in the wavelength range of 400-700 nm with a peak center at about 534 nm.

Three distinct excitation bands can be observed with maxima at 298, 330 and 399 nm, respectively, plus some weak excitation bands below 275 nm in the excitation spectrum of SrSiN₂ (Figure 6). These weak excitation bands below 275 nm originate from the host lattice, which has also been observed in the excitation spectra of Eu²⁺-doped MSiN₂ samples, as shown in the Figure 4. The remaining excitation bands in the wavelength range of 275-450 nm are assigned to Ce³⁺ transitions.

Fig. 6 shows the typical excitation and emission spectra of BaSiN₂: Ce, Li. The sample exhibits a broad emission band in the wavelength range of 400-700 nm with peak center at about 486 nm. Two distinct excitation bands are detected with maxima around 305 and 403 nm, respectively, plus some weak bands below the wavelength range of 275 nm. Similar to the case of SrSiN₂:Ce, Li, these weak excitation bands and the remaining excitation bands in the wavelength range of 275- 450 nm are assigned to the host lattice excitation and Ce³⁺ transitions, respectively. Since the absorption and the excitation bands of MSiN₂:Ce³⁺, Li⁺ perfectly match with the radiation of the GaN based LEDs in the range of 370-420 nm these materials, in combination with other phosphors are capable of generating white light.

Table 2 summaries the composition, phase characteristics and luminescence properties of Ce³⁺-doped MSiN₂ (M=Ca, Sr, Ba) for a comparison.

Table 2: Composition, phase characteristics and typical photoluminescence properties of Ce³⁺-doped MSiN₂ (M=Ca, Sr, Ba) at room temperature

MSiN ₂ :Ce ³⁺	M= Ca	M= Sr	M= Ba
Phase	CaSiN ₂	SrSiN ₂	BaSiN ₂
Crystal System	Face-centered cubic	P21/c	Cmca
Body color	Pink / red	Grey-White	Grey-White
Host lattice band gap (eV)	-	4.8	4.7
Absorption bands of Ce ³⁺ (nm)	450-550	370- 420	370- 420
Ce 5d excitation bands (nm)	365, 390, 440, 535	298, 330, 399	305, 403
Emission band maximum (nm)	625	534	486

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The emission and excitation spectra of a series of Mn²⁺-doped MgSiN₂ samples with different doping concentrations are presented in Figures 7 and 8.

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All Mg_{1-x}Mn_xSiN₂ phosphors with different Mn²⁺-doping concentration show a red emission band in the wavelength range of 550-800 nm with maxima from 626 to 655 nm with increasing Mn²⁺ concentration as can be seen from Fig. 7. This wavelength position of the emission band was unexpected because Mn²⁺ ion are supposed to be located in tetrahedrally coordinated sites of MgSiN₂ host lattice. Usually, the tetrahedral coordination of Mn²⁺ in oxide phosphors results in a green emission.

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Fig. 8 shows the excitation spectra. The short strong excitation band below 300 nm originates from the host lattice excitation as can also be shown for Eu²⁺ and Ce³⁺/Li⁺-activated MSiN₂

phosphors. The appearance of the host lattice excitation bands in the excitation spectrum of the Mn^{2+} emission indicates that there exists a efficient energy transfer from the host lattice to the Mn^{2+} ions, resulting in the typical red emissions of Mn^{2+} ions. This luminescence property makes this kind of inventive phosphor interesting for potential applications in the field of low-pressure mercury discharge lamps.

The remaining excitation bands in the wavelength range 300-500 nm can be assigned to the Mn^{2+} transitions. The absorption in this wavelength range can be improved by doping with suitable sensitizer ions.

The special advantage of the inventive phosphors consists in the improved chemical resistance against harmful environmental conditions. It could be proved by XRD measurements that the protecting layer formed by the described surface reaction method with $NH_4F \cdot HF$ mixtures consists of alkaline earth fluoride. The excellent effect of the protecting layer on chemical stability of the improved phosphors of invention is shown in Fig. 9 monitoring the relative emission intensity of uncoated and coated $MSiN_2:Eu^{2+}$ phosphor for a time period.

Therein, the emission intensities of coated and therefore stabilized $MSiN_2$ phosphor samples barely decrease compared with unprotected phosphor samples. Thus, a effective protection of $MSiN_2$ based phosphor can be realized.

Claims

1. An alkaline earth silicon nitride phosphor of the MSiN_2 type that is activated by Ce^{3+} and/or Eu^{2+} and/or Mn^{2+} ions.
5
2. The phosphor according to claim 1, wherein the phosphor is defined by the general formula $\text{MSiN}_2:\text{A}$, wherein M is a divalent metal ion, especially Mg, Ca, Sr, Ba, Be and/or Zn, and A is an activator chosen from the group Ce^{3+} , Eu^{2+} and/or Mn^{2+} .
10
3. The phosphor according to claim 1 or 2, wherein the phosphor is defined by one of the following formulas:
 $\text{SrSiN}_2:\text{Eu}^{2+}$, $\text{BaSiN}_2:\text{Eu}^{2+}$, $\text{SrSiN}_2:\text{Ce}^{3+}$, $\text{BaSiN}_2:\text{Ce}^{3+}$, $\text{SrSiN}_2:\text{Mn}^{2+}$
15 or $\text{BaSiN}_2:\text{Mn}^{2+}$.
4. The phosphor according to one of the claims 1 to 3, wherein the host lattice of the phosphor is represented by the formula: $\text{Sr}_{(1-x)}\text{Ba}_{(x)}\text{SiN}_2$, wherein $0 \leq x \leq 1$.
20
5. The phosphor according to one of the claims 1 to 4, wherein Si is partially replaced by Ge resulting in the following formula of the host lattice:
 $(\text{Sr}, \text{Ba})\text{Si}_{(1-z)}\text{Ge}_{(z)}\text{N}_2$ wherein $0 \leq z < 1$.
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6. The phosphor according to one of the claims 2 to 5, wherein Sr ions and/or Ba ions are partially replaced by divalent metal ions M like Mg, Ca, Zn, Be resulting in the following formula of the host lattice:
30 $(\text{Sr}, \text{Ba})_{(1-y)}\text{M}_{(y)}\text{SiN}_2$ wherein $0 \leq y \leq 1$.
7. The phosphor according to one of the claims 2 to 6, wherein $[(\text{Sr}, \text{Ba})\text{Si}]^{6+}$ is partially replaced by $(\text{LaAl})^{6+}$ resulting in the following formula of the host lattice:

(Sr, Ba)_(1-u)La_(u)Si_(1-u)Al_(u)N₂ wherein $0 \leq u < 1$, and wherein La is optionally replaced partially or completely by Sc, Y and/or a lanthanide, and wherein Al is optionally replaced partially or completely by B, Ga and/or Sc.

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8. The phosphor according to one of the claims 2 to 6, wherein [(Sr, Ba)Si]⁶⁺ is partially replaced by (NaP)⁶⁺ resulting in the following formula of the host lattice:

(Sr, Ba)_(1-v)Na_(v)Si_(1-v)P_(v)N₂ wherein $0 \leq v < 1$, and wherein Na is optionally replaced partially or completely by Li, K, Rb, and/or Cs.

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9. The phosphor according to one of the claims 2 to 6, wherein [(Sr, Ba)N]⁻ is partially replaced by (NaO)⁻ resulting in the following formula of the host lattice:

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(Sr, Ba)_(1-w)Na_(w)SiN_(2-w)O_(w) wherein $0 \leq w < 1$, and wherein Na is optionally replaced partially or completely by Li, K, Rb, and/or Cs.

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10. The phosphor according to one of the claims 2 to 9, wherein the ratio of Si to (Sr, Ba) is more than 1.

11. A white-light emitting LED comprising a light emitting element and a first phosphor according to one of the claims 1 to 9.

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12. The white-light emitting LED according to claim 11, wherein said first phosphor is further combined with red, yellow, green, and/or blue-emitting phosphors.

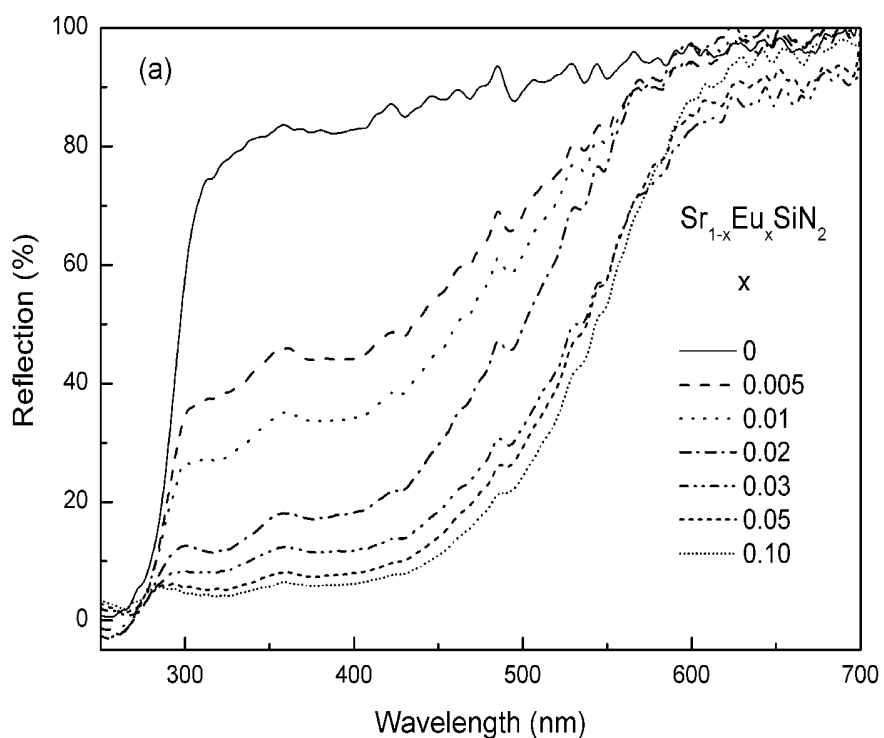


Fig. 1 (a)

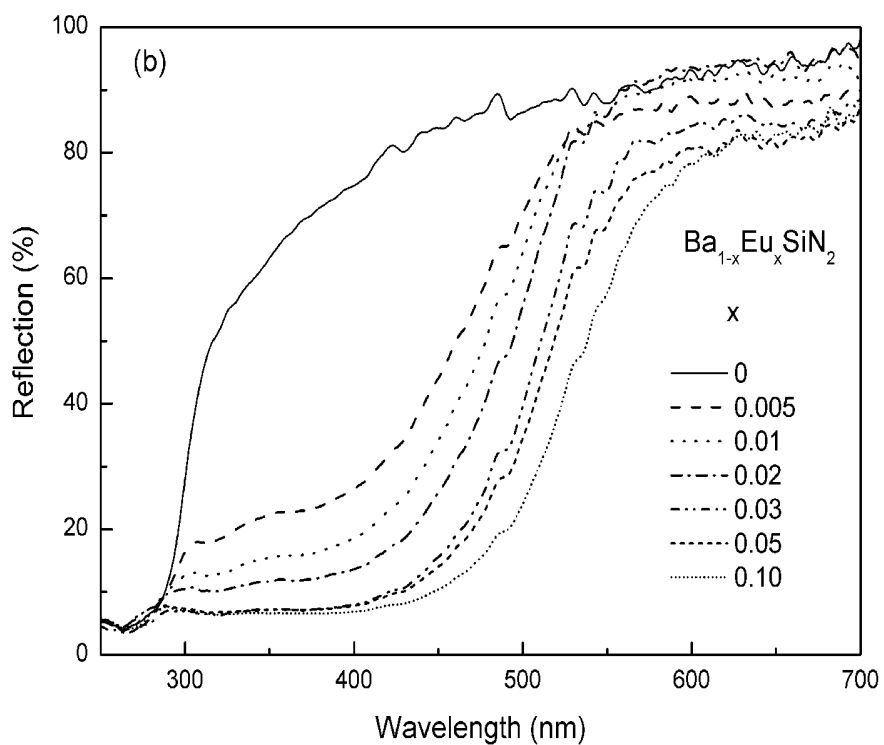


Fig. 1 (b)

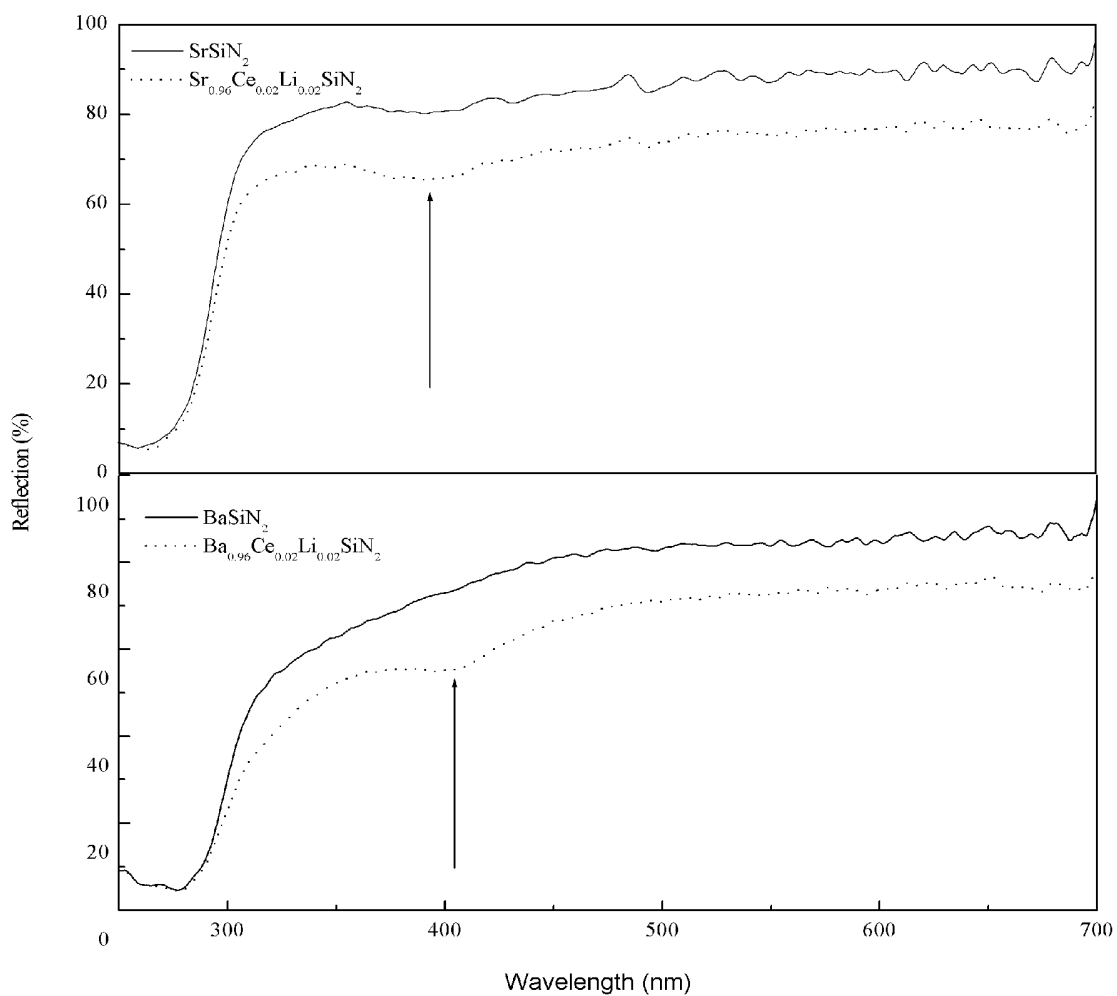


Fig. 2

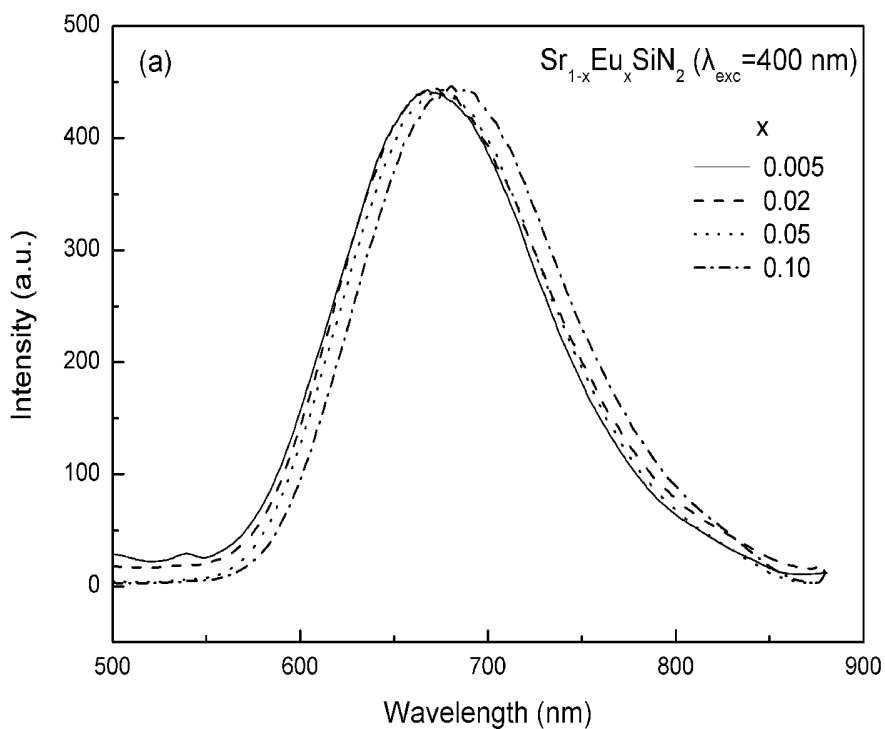


Fig. 3 (a)

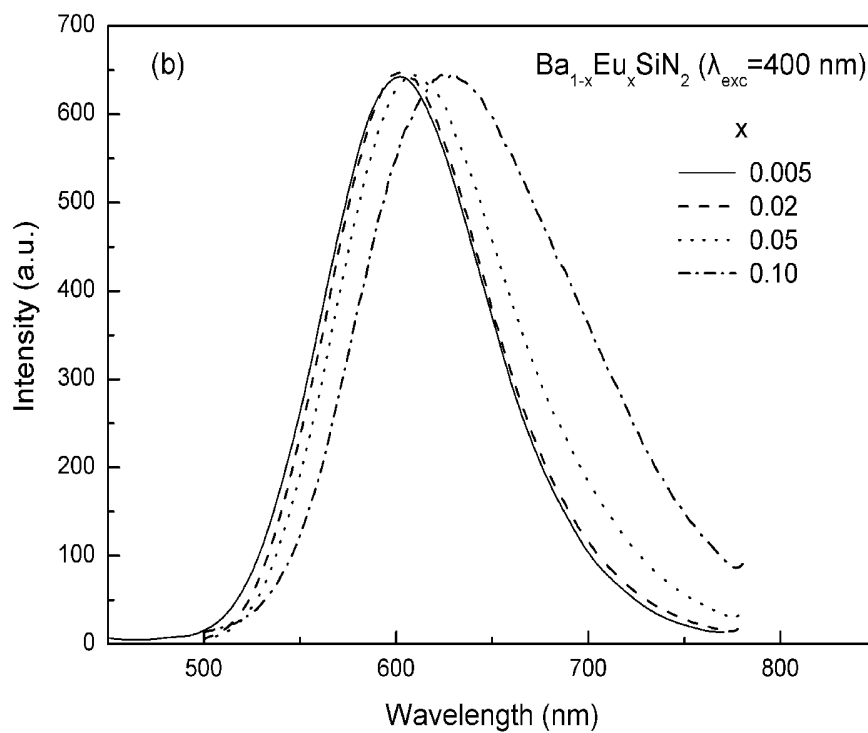


Fig. 3 (b)

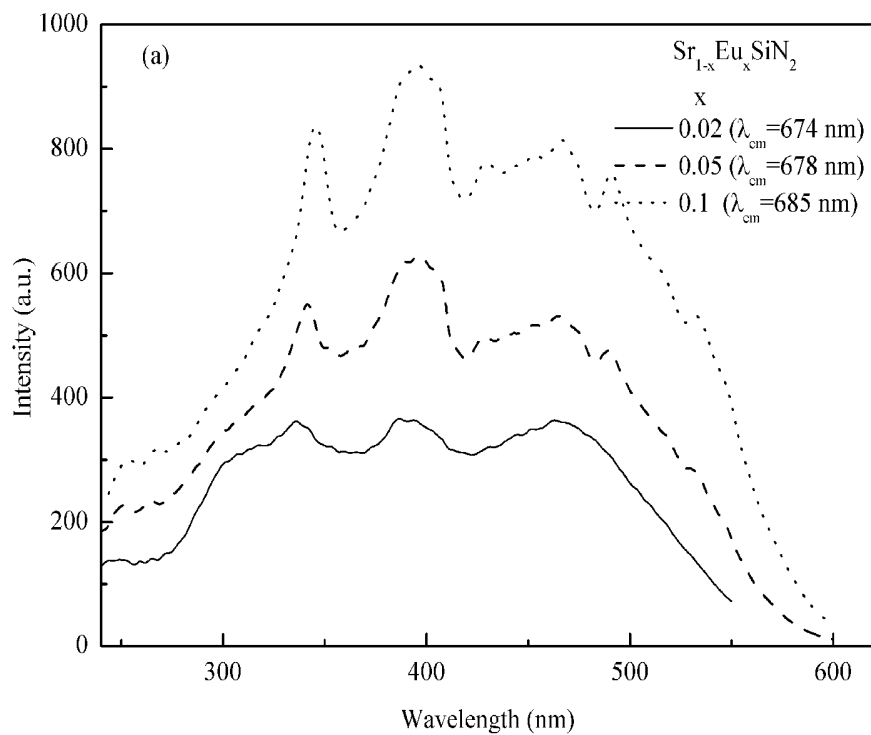


Fig. 4 (a)

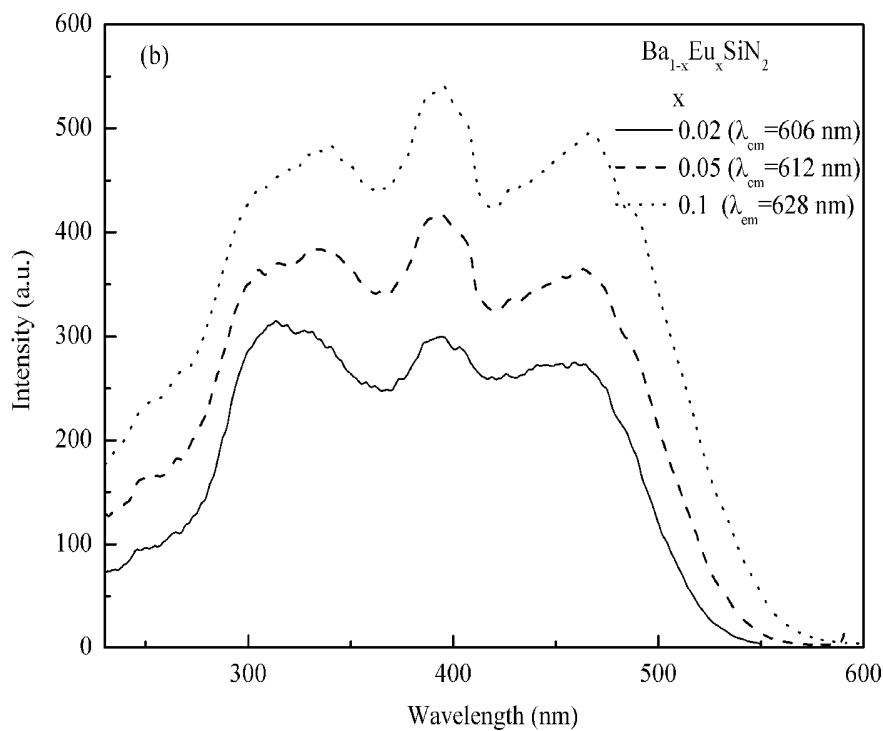


Fig. 4 (b)

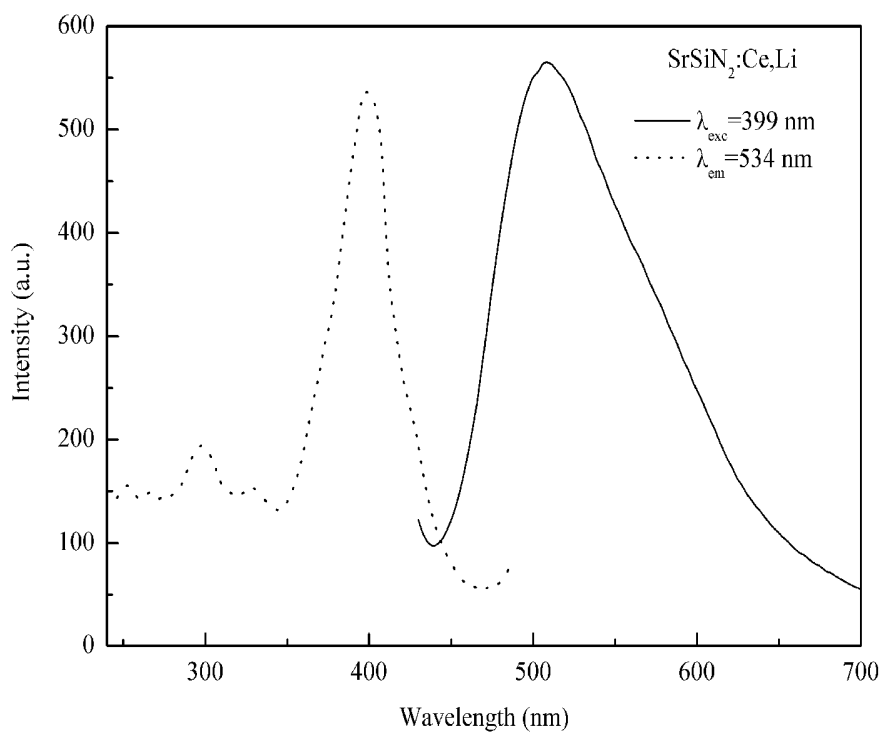


Fig. 5

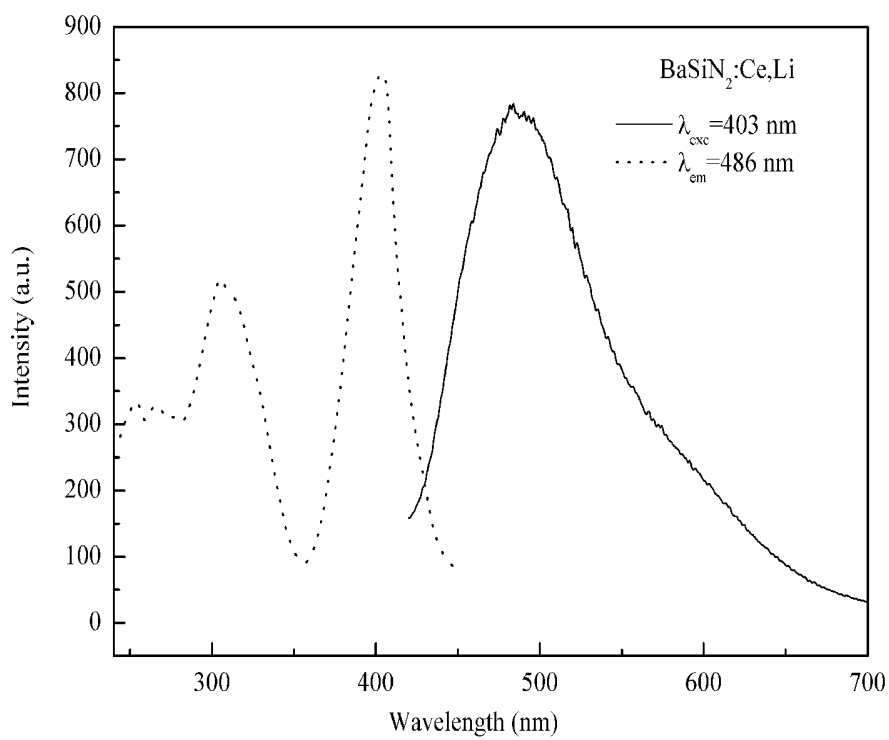


Fig. 6

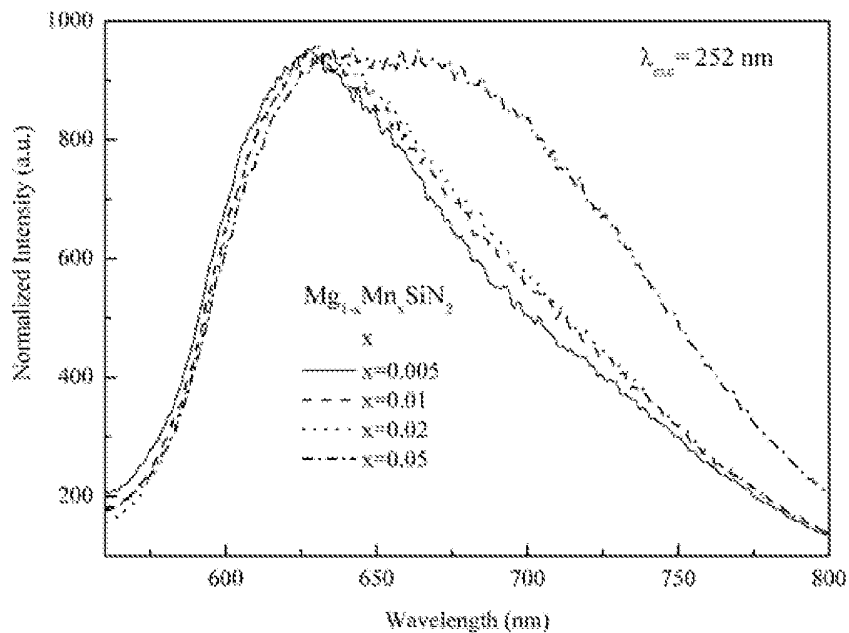


Fig. 7

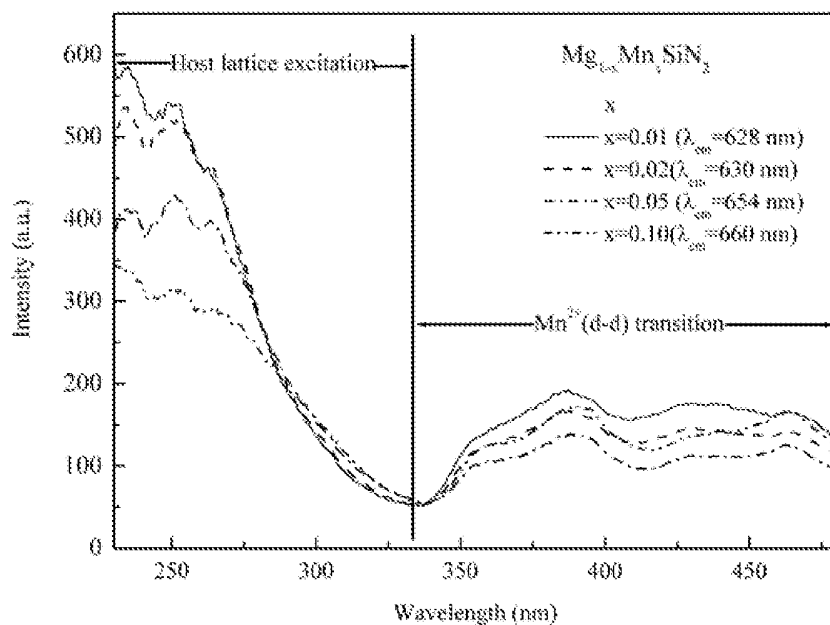


Fig. 8

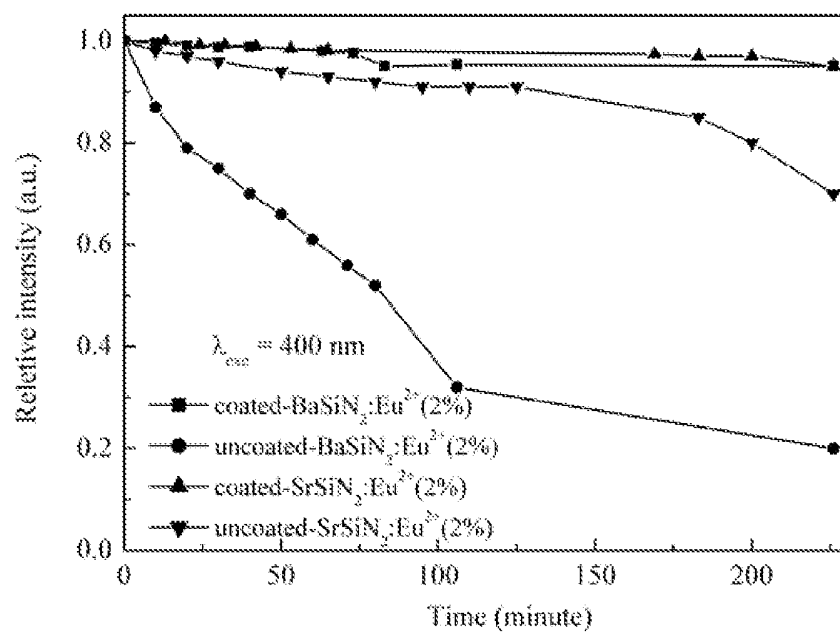


Fig. 9

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2008/058403

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C09K11/79 C09K11/59

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

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 practical, search terms used)

EPO-Internal, CHEM ABS Data, INSPEC, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/049763 A (MATSUSHITA ELECTRIC IND CO LTD [JP]; OSHIO SHOZO) 2 June 2005 (2005-06-02) examples 1-3 claims 1-17	1-12
X	US 2005/001225 A1 (YOSHIMURA NAOKI [JP] ET AL) 6 January 2005 (2005-01-06) paragraphs [0009], [0019], [0159], [0372], [0393] example 3 claims 1-26	1-12
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Further documents are listed in the continuation of Box C.

See patent family annex.

- * Special categories of cited documents :
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 - *O* document referring to an oral disclosure, use, exhibition or other means
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 - *&* document member of the same patent family

Date of the actual completion of the international search 14 October 2008	Date of mailing of the international search report 22/10/2008
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040. Fax: (+31-70) 340-3016	Authorized officer Kövecs, Monika
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/058403

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>BONDAR V ET AL: "Synthesis, Structure and Luminescence of A₂B₄C₅ Nitrides" MATERIALS RESEARCH SOCIETY SYMPOSIUM PROCEEDINGS,, vol. 639, 1 January 2001 (2001-01-01), pages G11.36.1-G11.36.6, XP002499469 the whole document</p> <p>-----</p>	1-12
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X	<p>UHEDA K ET AL: "Photo- and thermo-luminescence of zinc silicon nitride doped with divalent manganese" JOURNAL OF MATERIALS SCIENCE LETTERS,, vol. 20, 1 January 2001 (2001-01-01), pages 1753-1755, XP002499468 page 1753, line 13 - line 24 page 1753, line 9 - line 26</p> <p>-----</p>	1-12
X	<p>EP 1 104 799 A (PATRA PATENT TREUHAND [DE]) 6 June 2001 (2001-06-06) paragraph [0016] claims 1-8</p> <p>-----</p>	1-12

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