Title: RED EMITTING LUMINESCENT MATERIALS

Abstract: The invention relates to an improved red light emitting material of the formula \[ M \_x \_y A \_z \_x Si \_y \_x N \_y \_x O \_y \_x \]
whereby M is selected out of the group comprising Ba, Sr, Ca, Mg or mixtures thereof, A is selected out of the group comprising Al, Ga, B or mixtures thereof, RE is selected out of the group comprising rare earth metals, Y, La, Sc or mixtures thereof and x is >0 and y is >0 and <0.2. This material is believed to crystallize in a novel structure type that comprises two individual lattice sites for rare earth metal incorporation, which leads to an improved lighting behaviour.
RED EMITTING LUMINESCENT MATERIALS

FIELD OF THE INVENTION
The present invention is directed to novel luminescent materials for light emitting devices, especially to the field of novel luminescent materials for LEDs and their use in light emitting devices. The invention also relates to a light emitting device comprising such material and a system comprising light emitting devices.

BACKGROUND OF THE INVENTION
Phosphors comprising silicates, phosphates (for example, apatite) and aluminates as host materials, with transition metals or rare earth metals added as activating materials to the host materials, are widely known. As blue LEDs, in particular, have become practical in recent years, the development of white light sources utilizing such blue LEDs in combination with such phosphor materials is being energetically pursued.

Especially red emitting luminescent materials have been in the focus of interest and several materials have been proposed, e.g. US patent 6680569(B2), "Red Deficiency Compensating Phosphor for a Light Emitting Device", or from WO patent application 2005/052087 Al.

However, there is still the continuing need for red emitting luminescent materials which are usable within a wide range of applications and especially allow the fabrication of phosphor converted (pc) warm white pcLEDs with optimized luminous efficiency and color rendering.

SUMMARY OF THE INVENTION
It is an object of the present invention to provide a material which is usable within a wide range of applications and especially allows the fabrication of phosphor warm white pcLEDs with optimized luminous efficiency and color rendering.
This object is solved by a material according to claim 1 of the present invention. Accordingly, a material $\text{M}_{1-y}\text{A}_{y}\text{Si}_4\text{N}_7\text{X}_2\text{y}_0\text{x}_\pm\text{y}^{-}:\text{RE}$ is provided, whereby M is selected out of the group comprising Ba, Sr, Ca, Mg or mixtures thereof.

A is selected out of the group comprising Al, Ga, B or mixtures thereof.

RE is selected out of the group comprising rare earth metals, Y, La, Sc or mixtures thereof.

and $x \geq 0$ and $<1$, and $y \geq 0$ and $<0.2$.

It should be noted that by the term „$\text{M}_{1-y}\text{A}_{y}\text{Si}_4\text{N}_7\text{X}_2\text{y}_0\text{x}_\pm\text{y}^{-}:\text{RE}$“ especially and/or additionally any material is meant and/or included, which has essentially this composition.

The term "essentially" means especially that $\geq 95 \%$, preferably $\geq 97 \%$ and most preferred $\geq 99 \%$ 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, Si02 and the like and mixtures thereof.

Such a material has shown for a wide range of applications within the present invention to have at least one of the following advantages:

- Using the material as luminescent material, LEDs may be built which show improved lighting features, especially thermal stability.
- The material shows for a wide range of applications an exceptional high chemical stability because of the highly condensed nature of the host lattice
- The material for a wide range of applications only contains non-toxic and widely available constituents.

Without being bound to any theory, the inventors believe that the improved properties of the inventive material arise at least partially out of the structure of the material.

It is believed that the inventive material essentially has an orthorhombic structure which comprises three dimensionally connected $\text{SiN}_4$ and $\text{AlN}_4$ tetrahedra that are linked via corner and edge sharing. The $\text{AlN}_4$ tetrahedra build up trans-edge-
connected tetraheda chains running along crystallographic c direction that are cross-linked via corner-connecting SiN₄ tetrahedra. This leads to channels along c direction where the M cations are built in.

For a wide range of structures within the inventive material there seem to exist two crystallographically different "M"-sites (which are within this application called M(I) and M(2)) that are significantly different in size and number of coordinating N ligands. It is believed that red emission especially occurs after excitation of RE incorporated on the smaller M(I) site. Shorter wavelength RE emission resulting from RE on M(2) site may be reabsorbed by RE on M(I) site which then enhances the emission in the red spectral region, e.g. for many structures if RE comprises Eu(II).

For RE comprises Ce(III) it has been found for many structures that the emission are in the yellow-green spectral area; however, the shifts in the emission from one host structure to another are usually analogous to that if RE comprises Eu(II). In case RE comprises Pr(III), green and red emissions are frequently found, if RE comprises Tb(III), emissions are usually green and if RE comprises Sm(III), red emission occurs. For the two latter elements, in accordance with known prior art, the emission lines are for most structures independent of the host structure, since these latter two elements are line emitters.

In addition excitation energy absorbed by RE incorporated on the smaller M(I) site may be transferred to RE on M(I) site by means of energy transfer processes.

Because the M(2) site is large(r) and shows a high coordination number, larger M atoms (such as Ba) are preferentially built in on M(2) site, if they are present. Incorporation of such M atoms such as Ba has been shown to lead to a shift of emission to shorter wavelengths and a narrowing of the emission band for a variety of examples within the inventive material.

Because the M(I) site is smaller than the M(2) site and shows a low coordination number, smaller M atoms (such as Ca) atoms are preferentially built in on M(I) site. Incorporation of such M atoms such as Ca has been shown to lead to a shift of emission to longer wavelengths and a broadening of the emission band for a variety of examples within the inventive material.
Surprisingly as a result, the spectrum may be tuned by adjusting the Ba/Sr/Ca ratio in the lattice.

Further on, it has been found for a large variety of examples within the inventive material that a partial or complete replacement of the Al atoms located in the trans-edge-connected tetrahedra chains by Ga atoms leads to an expansion of the lattice, a reduction of the lattice phonon frequencies and thus to narrower emission bands.

According to a preferred embodiment of the present invention, RE is selected out of the group comprising Ce, Eu or mixtures thereof. In this context it is especially preferred that Eu is divalent (if present) and/or Ce is trivalent (if present).

According to a preferred embodiment of the present invention, the ratio (in mole:mole) of Europium and Cerium is >1:0.5 and <1:10, preferably >1:1 and <1:3, more preferred ≥1:1.5 and ≤1:3. This has been shown to be advantageous for a wide range of applications within the present invention.

According to a preferred embodiment of the present invention, the RE doping level is >0.05% and <10%.

This has been shown to lead to a material with further improved lighting features for a wide range of application within the present invention. Preferably, the doping level is >0.2% and <3%, more preferred >0.75% and <2%.

According to a preferred embodiment of the present invention, x is ≥0.01 and <0.2, preferably >0.05 and <0.1. This has been found to be advantageous for a wide range of applications within the present invention.

Without being bound to any theory, the inventors believe that with an increase of x a so called "flux effect" is also increased, which lowers the reaction temperatures needed to manufacture the inventive material.

However, an increase of x is also believed to widen the half-width of the emission band. This may be advantageous for some application within the present invention, especially if the material is doped with Ce(III) because a broad emission band in the green to amber spectral region is especially useful for a luminescent material used as color converter in white phosphor converted LEDs.
According to a preferred embodiment of the present invention, the photostability of the material is >80%, preferably >90%.

The term "photostability of X%" means and/or includes that if the material is irradiated with blue light at a flux density of 12 W/cm² and a phosphor temperature of 260°C, after 1 hour the intensity of luminescence is X% of the initial intensity.

The present invention furthermore relates to the use of the inventive material as a luminescent material.

The present invention furthermore relates to a light emitting material, especially a LED, comprising at least one material as described above.

Preferably the at least one material is provided as powder and/or as ceramic material.

If the at least one material is provided at least partially as a powder, it is especially preferred that the powder has a d₉₀ of >5 μm and ≤ 15 μm. Here, d₉₀ denotes a particle size, where 50% of the particles have a smaller (or larger) size as the d₉₀-value. This has been shown to be advantageous for a wide range of applications within the present invention.

According to a preferred embodiment of the present invention, the at least one material is at least partly provided as at least one ceramic material.

The term "ceramic material" in the sense of the present invention means and/or includes especially a crystalline or polycrystalline compact material or composite material with a controlled amount of pores or which is pore free.

The term "polycrystalline material" in the sense of the present invention means and/or includes especially a material with a volume density larger than 90 percent of the main constituent, consisting of more than 80 percent of single crystal domains, with each domain being larger than 0.5 μm in diameter and having different crystallographic orientations. The single crystal domains may be connected by amorphous or glassy material or by additional crystalline constituents.

According to a preferred embodiment, the at least one ceramic material has a density of >90% and ≤ 100% of the theoretical density. This has been shown to be advantageous for a wide range of applications within the present invention since then the
luminescence and optical properties of the at least one ceramic material may be increased.

More preferably the at least one ceramic material has a density of >97% and ≤100% of the theoretical density, yet more preferred >98% and ≤100%, even more preferred >98.5% and ≤100% and most preferred >99.0% and ≤100%.

According to a preferred embodiment of the present invention, the surface roughness RMS (disruption of the planarity of a surface; measured as the geometric mean of the difference between highest and deepest surface features) of the surface(s) of the at least one ceramic material is ≥0.001 µm and ≤5 µm.

According to an embodiment of the present invention, the surface roughness of the surface(s) of the at least one ceramic material is >0.005 µm and <0.8 µm, according to an embodiment of the present invention >0.01 µm and <0.5 µm, according to an embodiment of the present invention >0.02 µm and <0.2 µm, and according to an embodiment of the present invention >0.03 µm and ≤0.15 µm.

According to a preferred embodiment of the present invention, the specific surface area of the at least one ceramic material is >10^7 m^2/g and ≤0.1 m^2/g.

A material and/or a light emitting device according to the present invention may be of use in a broad variety of systems and/or applications, amongst them one or more of the following:

- Office lighting systems
- household application systems
- shop lighting systems,
- home lighting systems,
- accent lighting systems,
- spot lighting systems,
- theater lighting systems,
- fiber-optics application systems,
- projection systems,
- self-lit display systems,
- pixelated display systems,
- segmented display systems,
- warning sign systems,
- medical lighting application systems,
- indicator sign systems, and
- decorative lighting systems
- portable systems
- automotive applications
- green house lighting systems

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 at least one ceramic material for use in a light emitting device according to the invention as well as several embodiments and examples of a light emitting device according to the invention.

Fig. 1 shows a schematic perspective partial view of a structure of a host material according to a first example of the present invention;

Fig. 2 shows the structure of Fig 1 from a further perspective.

Fig. 3 shows a schematical view of the M(1)-site in the structure of the host material according to a first example of the present invention;

Fig. 4 shows a schematical view of the M(2)-site in the structure of the host material according to a first example of the present invention;
Fig. 5 shows a diagram of a Measured (above) and calculated (below) XRD pattern of a material according to a second example of the present invention; and

Fig. 6 shows a Emission spectrum (450 nm excitation) of a material according to a second example of the present invention;

The invention will be further understood by the following Examples I and II which - in a merely illustrative fashion - shows several materials of the present invention.

EXAMPLE I

Figs. 1 to 4 refer to SrAlSi₄N₇:Eu(2%) which was made according to the following:

SrAlSi₄N₇:Eu(2%) was prepared by mixing Sr metal powder (0.49 mol, 42.9 g), Eu metal powder (0.01 mol, 1.52 g), Si₃N₄ (grain size < 500 nm; 0.67 mol, 93.5 g) and AlN (1.0 mol, 41.0 g). The educts are heated in dry N₂ atmosphere in tungsten crucibles according to the following heating profile:

room temperature \(\rightarrow\) 3h \(\rightarrow\) 1630 °C \(\rightarrow\) 5h \(\rightarrow\) 1630 °C \(\rightarrow\) 1h \(\rightarrow\) 900 °C \(\rightarrow\) 45min \(\rightarrow\) RT

After firing, the phosphor powder is milled by ball milling and washed with water.

EXAMPLE II

Figs. 5 and 6 refer to SrAlSi₄N₇:Eu(3%) which was made analogous to SrAlSi₄N₇:Eu(2%) (cf. Example I)

Fig. 1 shows a schematic perspective partial view of the host material of the structure of Example I, i.e. SrAlSi₄N₇, Fig. 2 shows the same structure from another perspective. It can be clearly seen, how the SiN₄ and AlN₄ tetraeders form lattices.

The exact crystal data can be seen in Table I:
Table 1: Crystal data of SrAlSi$_4$N$_7$.

<table>
<thead>
<tr>
<th>chemical formula</th>
<th>SrAlSi$_4$N$_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>molar mass / g·mol$^{-1}$</td>
<td>325.03</td>
</tr>
<tr>
<td>crystal system</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>space group</td>
<td>Pna2$_1$ (No. 33)</td>
</tr>
<tr>
<td>lattice parameters / pm</td>
<td>$a = 1174.2(2)$, $b = 2139.1(4)$, $c = 496.6(1)$</td>
</tr>
<tr>
<td>cell volume / 10$^6$ pm$^3$</td>
<td>1247.2(4)</td>
</tr>
<tr>
<td>formula units in unit cell</td>
<td>4</td>
</tr>
</tbody>
</table>

Fig. 3 and Fig. 4 show the M(I) and M(2)-sites in the material of example I, i.e. SrAlSi$_4$N$_7$: Eu(2%). It can be clearly seen that the two sites are different which has the believed effects as described above.

The exact data for the host material (i.e. the undoped SrAlSi$_4$N$_7$) is given in Table II:

Table II: Atomic distances (pm) between M atoms and N ligands for SrAlSi$_4$N$_7$.

<table>
<thead>
<tr>
<th>Sr1-N1</th>
<th>250.3(5)</th>
<th>Sr1-N13</th>
<th>257.1(8)</th>
<th>Sr1-N10</th>
<th>263.4(6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr1-N13</td>
<td>270.1(8)</td>
<td>Sr1-N3</td>
<td>272.3(5)</td>
<td>Sr1-N12</td>
<td>314.2(5)</td>
</tr>
<tr>
<td>Sr2-N12</td>
<td>265.3(7)</td>
<td>Sr2-N8</td>
<td>270.9(5)</td>
<td>Sr2-N7</td>
<td>271.6(6)</td>
</tr>
<tr>
<td>Sr2-N11</td>
<td>282.1(6)</td>
<td>Sr2-N14</td>
<td>297.9(6)</td>
<td>Sr2-N12</td>
<td>301.1(7)</td>
</tr>
<tr>
<td>Sr2-N5</td>
<td>302.4(6)</td>
<td>Sr2-N6</td>
<td>305.7(6)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5 shows the measured and calculated XRD patterns (Cu-k\(\alpha\) radiation) of SrAlSi$_4$N$_7$: Eu (3%) indicating that a nearly phase pure material was prepared.

Fig. 6 shows the emission spectrum of SrAlSi$_4$N$_7$: Eu(3%) after excitation at 450 nm. A typical Eu$^{2+}$ 5d $\rightarrow$ 4f emission band is observed in the red spectral region.
As a comparison the spectroscopic properties of an inventive material is compared with prior art red phosphors in Table III:

Table III: Spectroscopic data of inventive and prior art materials.

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>Column 1</th>
<th>Column 2</th>
<th>LE (lm/W)</th>
<th>Rel. QE_{450} (%)</th>
<th>λ_{max} (nm)</th>
<th>FWHM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrAlSi₄N₇:Eu (INVENTIVE)</td>
<td>0.636</td>
<td>0.362</td>
<td>177</td>
<td>100%</td>
<td>634</td>
<td>100</td>
</tr>
<tr>
<td>(Ba,Sr)₂Si₂N₈:Eu (COMPARISON)</td>
<td>0.613</td>
<td>0.386</td>
<td>242</td>
<td>93%</td>
<td>620</td>
<td>95</td>
</tr>
<tr>
<td>CaSiAlN₃:Eu (COMPARISON)</td>
<td>0.668</td>
<td>0.332</td>
<td>118</td>
<td>97%</td>
<td>649</td>
<td>98</td>
</tr>
</tbody>
</table>

It can be seen that the inventive material shows comparable, sometimes even improved lighting properties as compared with the comparative materials. The value given under column 1 and 2 of table III denote the values for the x- and y-color coordinates in the CIE diagram, respectively.

A warm white emitting pcLED light source may be built up by combining the inventive material with e.g. a yellow emitting Y₃xAl₃O₁₂:Ceₓ color converting material and a blue emitting AlInGaN pump LED.

As a further - merely illustrative - example, 10 - 20 wt% of SrAlSi₄N₇:Eu were mixed with 80 – 90 wt% Y₃Al₅O₁₂:Ce, suspended in a silicone resin and deposited on top of an AlInGaN LED die emitting at 440 - 460 nm. The composition and thickness of the phosphor layer was adjusted to realize a white pcLED lamp with a correlated color temperature of 3200K.

Table IV compares the efficiency and color rendering properties of such a lamp with comparative examples that are built up with prior art red phosphors. It is shown that the claimed phosphor system allows the fabrication of white LED lamps that combine both, a high luminous efficiency and an illumination grade color rendering. Ra is the average color rendering index, R9 is the color rendering index of "red".
TABLE IV:
Efficiency and color rendering properties

<table>
<thead>
<tr>
<th>Red phosphor component</th>
<th>Rel. luminous efficiency</th>
<th>Ra</th>
<th>R9</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrALSi₅N₇:Eu</td>
<td>89%</td>
<td>79</td>
<td>15</td>
</tr>
<tr>
<td>(INVENTIVE)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Ba,Sr)₂Si₅N₃:Eu</td>
<td>100%</td>
<td>70</td>
<td>-</td>
</tr>
<tr>
<td>(COMPARISON)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaSiAlN₅:Eu</td>
<td>77%</td>
<td>90</td>
<td>70</td>
</tr>
<tr>
<td>(COMPARISON)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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. 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. Material of the formula $\text{M}_{i+y}\text{A}_{i+x}\text{Si}^{4-}\text{N}_{7-x}2\text{yO}_{x+2}\text{y}^{0+x}:\text{RE}$, whereby
   M is selected out of the group comprising Ba, Sr, Ca, Mg or mixtures thereof
   A is selected out of the group comprising Al, Ga, B or mixtures thereof
   RE is selected out of the group comprising rare earth metals, Y, La, Sc or mixtures thereof
   and $x$ is $\geq 0$ and $\leq 1$ and $y$ is $\geq 0$ and $< 0.2$

2. The material of claim 1, whereby RE is selected out of the group comprising Eu, Ce or mixtures thereof.

3. The material of claim 1 or 2, whereby the RE doping level is $> 0.05\%$ and $< 10\%$.

4. The material of any of the claims 1 to 3, whereby the photostability of the material is $> 80\%$, preferably $> 90\%$.

5. Use of a material according to any of the claims 1 to 4 as a luminescent material.

6. Light emitting device, especially a LED comprising at least one material according to any of the claims 1 to 4.

7. The light emitting device of claim 6 whereby the at least one material is provided as powder and/or as ceramic material.
8. The light emitting device of any of the claims 5 to 7 whereby the powder has a dso of >5 µm and ≤ 15 µm.

9. The light emitting device of any of the claims 6 to 8, whereby the ceramic has >90% of the theoretical density.

10. A system comprising a material according to any of the claims 1 to 4 and/or a light emitting device according to any of the claims 6 to 9 and/or making use according to Claim 5, the system being used in one or more of the following applications:
   - Office lighting systems
   - household application systems
   - shop lighting systems,
   - home lighting systems,
   - accent lighting systems,
   - spot lighting systems,
   - theater lighting systems,
   - fiber-optics application systems,
   - projection systems,
   - self-lit display systems,
   - pixelated display systems,
   - segmented display systems,
   - warning sign systems,
   - medical lighting application systems,
   - indicator sign systems, and
   - decorative lighting systems
   - portable systems
   - automotive applications
   - green house lighting systems
FIG. 3

FIG. 4
A. CLASSIFICATION OF SUBJECT MATTER

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

B. DOCUMENTS 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 international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
</table>

X Further documents are listed in the continuation of Box C.

X See patent family annex.

Special categories of cited documents:

'A' document defining the general state of the art which is not considered to be of particular relevance

'E' earlier document but published on or after the international filing date

'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

'P' document published prior to the international filing date but later than the priority date claimed

'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

'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

'A' document member of the same patent family

Date of the actual completion of the international search

21 May 2008

Date of mailing of the international search report

06/06/2008

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016

Authorized officer

Doslik, Natasa
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>MUELLER-MACH R ET AL: &quot;NITRIDOSILICATES, A NEW FAMILY OF PHOSPHORS FOR COLOR CONVERSION OF LEDS&quot; PROCEEDINGS OF THE SPIE, SPIE, BELLINGHAM, VA, vol. 5941, 1 January 2005 (2005-01-01), pages 1-08, XP008062540 ISSN: 0277-786X pages 4-6</td>
<td>1-10</td>
</tr>
</tbody>
</table>
Continuation of Box II.2

Claims Nos.: 1-10 partially

The present claims 1-10 relate to an extremely large number of possible compounds and products. Support and disclosure in the sense of Article 6 and 5 PCT is to be found however for only a very small proportion of the compounds and products claimed, namely only nitridosilicates, as disclosed in the examples 1-2 of the description. The non-compliance with the substantive provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extent of the search of claims (PCT Guidelines 9.19 and 9.23).

The search of claims was restricted to those claimed compounds and products which appear to be supported and a generalisation of their structural formulae, namely those nitridosilicates as disclosed in the description and in the general formula of claim 1, excluding the oxonitridosilicates (which are also claimed).

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2)PCT declaration be overcome.
Box No. II  Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. ☑ Claims Nos.: 1-10 partially
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
   see FURTHER INFORMATION sheet PCT/ISA/210

3. ☑ Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III  Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest
☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
☐ No protest accompanied the payment of additional search fees.
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