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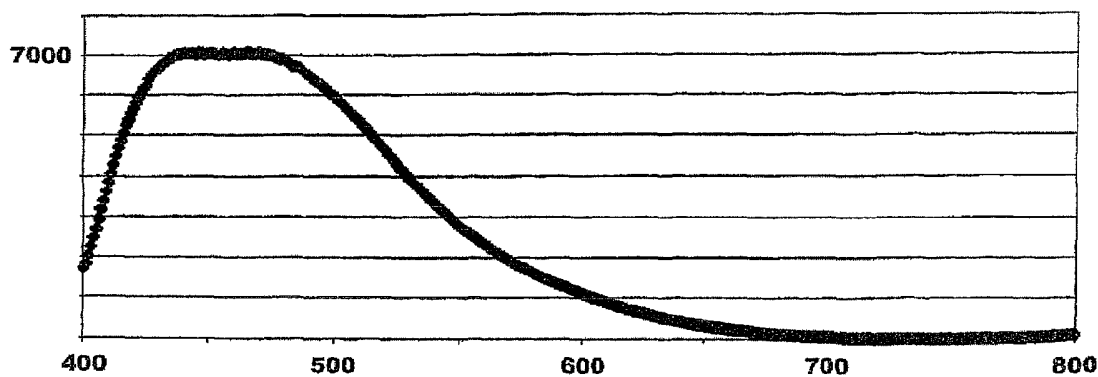
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(54) Title: NOVEL MATERIALS USED FOR EMITTING LIGHT



(57) Abstract: An luminescent composition comprises a mixture of two or more materials, emitting electromagnetic radiation when subject to stimuli, wherein the spectral emission is not calculable at a first approximation as the simple weighted sum of the spectral emissions of the materials independently subject to said stimuli. Especially advantageous compositions are achieved if the anionic matrix is an oxide and the doping anionic salt is a fluoride or vice versa.

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Frank Kubel

"I-PCT"

NOVEL MATERIALS USED FOR EMITTING LIGHTTechnical Field of the Invention

The invention relates to a material emitting electromagnetic radiation, particularly visible light, when provided with a stimulus.

Technical Background

It is known that certain materials, including natural minerals, emit electromagnetic radiation, particularly visible light (electromagnetic radiation in the human-visible part of the spectrum, wavelengths approximately 400nm-700nm), when provided with an appropriate stimulus. This stimulus can be electromagnetic radiation of a differing nature, normally of a lower wavelength (higher frequency), where the phenomenon is termed fluorescence or phosphorescence, and where the energizing radiation may be e.g., ultra-violet light: the stimulus may also be of e.g., energetic electrons or ions, the former involving either direct (electrical circuit) or indirect (electron bombardment) electrical contact. Other stimuli are also possible.

For the purposes of lighting, particularly the lighting of interior or partially enclosed spaces, it has for a long time been desirable to find or create materials which, singly or in mixtures, produce white light in the human visible region. Many such materials have been found, but they have tended to be regarded as less than ideal because of consideration of longevity, spectral shift over time, limited range of conditions of use, etc. Consequently the search for improved materials continues.

One particular application for which improved materials are re-

quired is that of fluorescent lamp bulbs. These (usually a solid solution of Mn & Sb in calcium fluoroapatite) currently work by means of ionic bombardment and/or ultraviolet light stimulation from a gas containing mercury vapour. Mercury is classified as a hazardous material, and it is desirable (and, indeed, in some legal jurisdictions, mandated) that the manufacture and use of lamp bulbs containing mercury should cease once a suitable (economically sensible, and environmentally less damaging) substitute is found, e.g., a fluorescent lamp bulb which works with nitrogen gas and noble gas without using mercury vapour. One problem with implementing this change is that the known and existing phosphors, largely developed for use with mercury vapour, do not perform well in other systems.

Fluorescent oxide systems are well known, as are fluorescent halide systems, particularly barium halide systems. The doping of oxides with oxides is also well known, and the doping of fluorides with fluorides to create e.g., barium (mixed halide) systems such as BaFCl has also been disclosed as is the further doping of such systems with rare earth elements - BaFCl doped with Sm(II) is a classic, stable, red fluorescent material. It is mentioned in US 5,543,237, that a material with a cross-doping of fluorides with oxides might create a fluorescent oxide system, although all embodiments in said document relates to doping of fluorides with fluorides.

Most systems known and studied which are capable of electromagnetic radiation emission under certain stimuli are oxides, where the number of disclosures is great. For instance, a new blue-white material, Sr_2CeO_4 (and its Eu-doped form) were announced by Symyx in 1998 after having tested 25,000 rare earth mixed oxides for fluorescence using combinatorial chemistry.

The class of materials which does not use oxides but which uses halides has received much less study, but has been previously disclosed. Much of this work has concentrated on substitution of halides and doping in the system BaF_2 , a well-known phosphorescent material, to create hitherto unknown structures, superlattices and consequent effects.

The use of mixed halides, in particular the use of chlorine and fluorine together, has been disclosed to a limited extent. In 1997 a group at the Department of Physical Chemistry at the University of Geneva, including Prof. Hans Bill and Prof. Frank Kubel, filed for and subsequently obtained a patent (WO 99/17340, priority date 29.9.1997) and published structures in 1998, showing new white fluorescent materials (and devices based on them) based on the barium-7 system, particularly $\text{Ba}_7\text{F}_{12}\text{Cl}_2$, these specifically being of the nature $\text{Ba}_{7-x-y}\text{M}_x\text{Eu}_y\text{F}_{12}\text{Cl}_u\text{Br}_v$ where M is one of Ca, Mg, Sr and Zn, and x, u and v are in the range 1-2, with $u+v=2$, and y is between 0.00001 and 2. This patent thus also discloses the use of triple mixed halides, and of double doping, within the limited range of the Ba-7 system and where one of the dopants is Eu and where the second dopant is one of Ca, Mg, Sr and Zn. This is the only known material which works with nitrogen gas (as the main constituent - some noble gases e.g., Ar, Xe, are used in the mixture for control purposes) in fluorescent lamps. The same group published in 1999 work on the barium-12 system, particularly $\text{Ba}_{12}\text{F}_{19}\text{Cl}_5$. This work discussed a class of materials involving barium (mixed halides) where primary doping, with Europium, has been disclosed. The barium-1, barium-7 and barium-12 systems are those known within the barium halide systems.

Summary of the invention

Based on the above mentioned prior art it is an object of the

invention to provide a better fluorescent material. A further object is to provide a better material for a luminescent composition. A further object is to provide a method to induce emission of electromagnetic radiation.

The inventors have the insight that the light emission from these structures is, in the absence of (weak) effects caused by defects, caused by the introduction of doping elements, for preference rare-earth cations, for preference europium: however these rare-earth cations must reside in a position in the lattice which is strongly polar i.e., non-centro-symmetric, to show strong optical character and confer this on the material as a whole.

There are various means of preparing such structures, which either rely on introducing the dopant cation into the matrix in its final form, or introducing it in a different chemical form and then converting it *in situ*. In the case of europium, where the Eu^{2+} cation is desired, the second route is favoured, the Eu being introduced as Eu(III) (during e.g., precipitation of the main structure) and then reduced *in situ* by a reduction step at 700°C or directly by doping with stable EuF_2 .

Other examples of fluorescent materials include (all doped with Eu^{2+}) Ba_2SiO_4 doped with Eu^{2+} , Sr_2SiO_4 , SrAlF_5 , BaMgF_4 (blue), BaSiO_3 , BaMgF_4 , SrMgF_4 (blue), and SrAlF_5 , $\text{Ba}_6\text{Mg}_7\text{F}_{26}$ (blue to white) and all solid solutions within this system.

This disclosure adds and claims the following new materials:

- The strontium aluminate, SrAl_2O_4 system doped with Eu^{2+} (as either the oxide or the fluoride) shows bright white emission.
- Strontium aluminum silicates, notably $\text{Sr}_2\text{Al}_2\text{SiO}_7$, $\text{SrAl}_2\text{Si}_2\text{O}_8$, and $\text{Sr}_3\text{Al}_{10}\text{SiO}_{20}$ (this last a new compound), doped with Eu^{2+} , which

show respectively orange/green, weak red, and yellow luminescence under 254nm and 366nm UV stimulation.

All of the above work has, however, proceeded upon direct substitutional lines: that is, the introduction in principle of a single new element e.g., europium, into a pre-existing crystal (or the forming of the same *in situ*), without introducing disruption via the anion; thus using europium fluoride as substituent into fluoride matrices, or europium oxide into oxide matrices. The choice of the counter-ion of the dopant has always conventionally been the same as the dominant anion of the matrix, to allow ease of fabrication with minimal disruption. The limited use of double doping has proceeded along the same lines.

The disadvantage of this approach is that it is now known that, in order for the doped rare earth cation e.g., europium, to be optically active, as noted above, it must reside in an area of local symmetry which is decidedly polar, i.e., non-spherically-symmetric. Direct doping or that with matching anions does not provide this to any dependable extent; doping with other cations (e.g., dysprosium as well as europium) does to some extent. However, since it has been shown by recent work that substances such as europium fluoride EuF_2 diffuse as a linked pair within structures, it follows that doping using such a pair structure within a matrix or crystal lattice of differing anionic structure must necessarily create a strongly polar local symmetry for the Eu cation (the F taking up an adjacent oxide position within the local lattice). Thus in particular, oxides doped with fluorides show strong optically active properties. This is important because although generally the fluorides show strong optical activity, they tend to be, as noted above, unstable over time: the oxides are much more stable but show weaker effects. By the present means the virtues of the two systems can be simultaneously

expressed, a further advantage being that low levels of pair-doping (because the doping occurs as pairs) is needed to manifest a strong optical effect.

The observations in such systems are recent, and so the exact nature of the chemical compounds and their structures are still the subject of theory and academic debate, but their exact nature does not prevent or predetermine this disclosure. It should be noted that, unlike many classical material systems, the optically active systems, like their natural counterparts, are difficult to describe in precise crystallographic terms, their optical activity and thus their usefulness arising rather from the irregularities and defects in the structures than from any regular features.

The present disclosure is thus for an entirely novel class of materials which are capable of emitting electromagnetic radiation under appropriate stimuli. Notwithstanding any other potential uses of the materials, e.g., to emit light under electronic or electromagnetic stimulation, one particular disclosure is that certain of these materials demonstrate the desirable characteristics of stable emission under ultra-violet light / ionic stimulation from ions other than those arising from mercury vapour, thus permitting stable white light produced by fluorescence without involving the use of mercury.

The novel class of materials in particular includes those obtained by the use of doping oxides with fluorides, possibly also using further doping elements.

This disclosure thus claims all novel systems obtained by cross-doping of anions, in particular the doping of fluorides into oxides, together with the use of doping using one or more further

elements in them, and the novel class of materials obtained by this use of doping. It further claims the emission of electromagnetic radiation from such materials under suitable stimuli, and devices incorporating these materials and effects.

Synthesis of the systems studied is made by ceramic methods from reagent grade starting materials in inert (corundum, platinum, graphite) crucibles. Reduction is made in a nitrogen-hydrogen furnace.

Short description of the drawings

- Fig. 1 shows the emission spectrum on 330 nanometer excitation for a phase mixture of above mentioned $\text{Ba}_{12.25}\text{Al}_{21.5}\text{Si}_{11.5}\text{O}_{66}$ / $\text{BaAl}_2\text{Si}_2\text{O}_8$ / BaAl_2O_4 .
- Fig. 2 shows the spectrum of said system with its intensity in relative strength (y-axis) against the wavelength in nanometer (x-axis).
- Fig. 3 shows three X-ray diffraction spectra for $\text{Ba}_{13.3}\text{Al}_{30}\text{Si}_6\text{O}_{70}$, one measured spectrum, one simulated spectrum and the difference spectrum.
- Fig. 4 shows three X-ray diffraction spectra for Ca_2SiO_4 , one measured spectrum being almost identical to a simulated spectrum and the difference spectrum.
- Fig. 5 shows three X-ray diffraction spectra for $\text{Ba}_{12.25}\text{Al}_{20.5}\text{Si}_{11.5}\text{O}_{66}$, one measured spectrum, one simulated spectrum and the difference spectrum.
- Fig. 6 shows three X-ray diffraction spectra for Ba_2SiO_4 , one measured spectrum being almost identical to a simulated spectrum and the difference spectrum.
- Fig. 7 shows three X-ray diffraction spectra for Sr_2SiO_4 , one measured spectrum being very similar to a simulated spectrum and the difference spectrum.
- Fig. 8 shows the emission spectrum on 254nm excitation for SAS

doped with Eu.

Fig. 9 shows a X-ray diffraction spectrum for the blue emitting SAS phase showing pure powder.

Fig. 10 shows emission for sample GW004.

Fig. 11 shows an excitation spectrum of sample W1; and

Fig. 12 shows an emission spectrum of sample W1.

Detailed description of exemplary embodiments

To demonstrate the validity of this approach a wide number of systems have been studied, which include:

- The alkaline earth ortho-silicates, notably Ca_2SiO_4 , Sr_2SiO_4 and Ba_2SiO_4 , doped with Eu^{2+} , where the dopant may be either the fluoride or the oxide of the rare earth metal (to show the fluoride-into-oxide heteroatom effect), the dopant concentration ranges between 0.5mol% to 2.5mol%, the calcination temperature ranges between 700°C and 900°C, and the reduction temperature ranges between 900°C and 1100°C.
- In the Ba_2SiO_4 system, the emission under 254nm and 366nm UV is notably shifted towards higher wavelengths for the fluoride-doped systems, at all doping levels, with this being more pronounced at combination of the lowest calcination temperature and the highest reduction temperature (strong green).
- In the Sr_2SiO_4 system, the fluoride doping universally shifts the emission towards higher wavelengths.
- The alkaline earth simple silicates XSiO_3 and X_3SiO_5 (X is preferably Ba, Ca or Sr), doped with europium fluorides, showed mainly dark red emission.
- The mixed alkaline earth / metallic earth silicate systems XYSiO_4 , XYSi_2O_6 , $\text{X}_2\text{YSi}_2\text{O}_8$, X_3YSiO_7 and $\text{X}_3\text{YSi}_4\text{O}_{12}$, where Y is an alkaline earth chosen from preferably Ba, Sr, and Ca, and X is a metal such as Mg or Zn, where the final mixtures can be a mixture of any number of phases according to the above formulae, where in all cases doping was achieved by fluorides. These all

show luminescence. Particular examples include:

No.	System	Dopant	UV wavelength	UV wave-length
			254nm	366nm
28	$\text{Sr}_3\text{MgSi}_2\text{O}_8$, $\text{Sr}_2\text{MgSi}_2\text{O}_7$, MgO	Eu^{2+}	Orange	absorbing
30	$\text{Ca}_2\text{ZnSi}_2\text{O}_7$, Zn_2SiO_4 , ZnO, $\text{Ca}_3\text{ZnSi}_2\text{O}_8$ (?)	Eu^{2+}	Grey	grey
31	SrSiO_3 , $\text{Sr}_3\text{MgSi}_2\text{O}_8$, $\text{Sr}_2\text{MgSi}_2\text{O}_7$, SiO_2	Eu^{2+}	pale pink	blue
32	BaSiO_3 , BaMgSiO_4 , SiO_2 , MgO	Eu^{2+}	pink	pale blue
34a	BaSiO_3 , BaZnSiO_4 , SiO_2 , ZnO	Eu^{2+}	greenish yellow	yellow
34b	BaSiO_3 , BaZnSiO_4 , SiO_2 , ZnO	Eu^{2+}	green	yellow

- It should be noted that various other phases were created as part of this exercise which lie beyond the simple formulae given above. A new compound, $\text{Ca}_3\text{ZnSi}_2\text{O}_8$ was found as part of this synthesis.

- The mixed aluminates e.g., $\text{Sr}_3\text{AlO}_4\text{F}$, $\text{Sr}_6\text{Al}_{12}\text{O}_{32}\text{F}_2$, $\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}\text{Cl}_2$, $\text{Ca}_8(\text{Al}_{12}\text{O}_{24})(\text{WO}_4)_2$, (all doped with Eu) - all showed red luminescence

- The yttrates and gallates such as SrY_2O_4 , SrGa_2O_4 , MgGa_2O_4 - showed red luminescence except the Mg variants, which showed green

- The borates such as $\text{Ba}_2\text{Zn}(\text{BO}_3)$, $\text{BaZn}_2(\text{BO}_3)_2$ and $\text{Ba}_2\text{Zn}(\text{B}_3\text{O}_6)_2$ (and the Mg and Ca substituted for Zn variants) - showed red/orange luminescence

- The fluorides including BaMgF_4 , SrMgF_4 and $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ doped with in this case the oxides of Sm and Eu.

- BaMgF₄ (doped Sm²⁺) shows intense red
- BaMgF₄ (doped Eu²⁺) shows intense blue
- Ba₇F₁₂Cl₂ (doped Eu(II) + Na) shows intense white

It is possible to add or replace within all alkaline earth systems mentioned above the alkaline earth by alkaline systems.

The use of alkali flux to introduce either alkali as an dopant and/or the disorder which this introduction promotes to obtain white light rather than the blue which would be obtained in its absence is a new insight and not noted within the prior art, e.g. WO 99/17340.

It should be noted in particular that one method of obtaining a good white light source is to combine a blue/UV emitting light-emitting diode (LED) with suitable phosphor material(s) and, optionally, other light absorbing materials such as colored coatings. It is a particular feature of this invention that the choice of blue/UV LED and/or light absorbing materials are critically dependant on the light-absorbing and reemitting characteristics of the phosphor materials to the extent that two similar UV LEDs with identical specifications for peak wavelength emitted will lead to quite different light-emitting properties of the system as a whole, where these properties re not predictable from the UV LED specifications.

The various single- and multiple-component systems studied included with UV LED stimulation at nominal wavelengths between 350-405nm:

Ba₂Si₂O₈ doped with SmF₃ - gives a lilac light

BaAl₂O₄ doped with Pr - gives a blue light

SrAl₂O₄ doped with Pr³⁺ - gives a deep green / blue light

SrAl₂O₄ doped with Ho³⁺ - gives a dark blue /violet light

SrAl₂O₄ / SrAl₁₂O₁₉ - gives deep green / blue light

$\text{Sr}_3\text{Al}_{20}\text{SiO}_{40}$ / $\text{SrAl}_2\text{Si}_2\text{O}_8$ - gives a violet light

$\text{SrAl}_2\text{Si}_2\text{O}_8$ / SrSiO_3 / $\text{SrAl}_{12}\text{O}_{19}$ doped with Eu^{2+} - gives a blue light

$\text{SrAl}_2\text{Si}_2\text{O}_8$ / SrSiO_3 / $\text{SrAl}_{12}\text{O}_{19}$ doped with La^{3+} - gives a blue light

$\text{BaAl}_2\text{Si}_2\text{O}_8$ - gives a deep blue / violet light

$\text{Ba}_{12.25}\text{Al}_{21.5}\text{Si}_{11.5}\text{O}_{66}$ / $\text{BaAl}_2\text{Si}_2\text{O}_8$ / BaAl_2O_4 - gives a blue light (but see below)

Also claimed is a second and separate observation and the applications thereof. Up till now it has however been observed that if a mixture of two or more materials capable of emitting light in such fashion are stimulated by a means which would cause each independently to emit light, then the spectrum which results from the mixture can be determined by the independent natures and quantities of the two or more materials present. In short the emission spectrum from the mixture is reliably to a first approximation the simple weighted sum of the emissions from the individual parts, summed according to their fractional composition of the mixture, where this fractional composition may be based on e.g., mass, volume, or surface area of the components without great difference.

This understanding is used in the commercial manufacture of many lighting sources, which take as the basis for their design the assumption that if a mixture of materials is used those materials essentially act independently. This assumption has served the lighting industry well.

What has not yet been observed, and which is therefore novel and is the subject of this disclosure, is that of a mixture of two or more materials emitting light where the emitted light is NOT the simple weighted sum of the individual components provided by the individual materials independently subject to the stimulus, whatever approach to fractional composition is taken as noted

above, but is significantly different.

In such cases the emitted light spectrum is not calculable by such means. In particular it is not calculable by the simple approach because the emitted spectrum from the mixture shows high emissions at wavelengths which are not typical of each of the components considered singly.

To give a specific example: a mixture of three materials, $\text{Ba}_{12.25}\text{Al}_{21.5}\text{Si}_{11.5}\text{O}_{66}$ / $\text{Ba}_2\text{Si}_2\text{O}_8$ / BaAl_2O_4 (proportions around 26% / 22% / 52%), each of which would independently emit a narrow spectrum of green visible light (around 480nm) when subject to a given ultra-violet light stimulus, when created in a mixed form and reduced, do not give a green light as those conversant with the art would have predicted, or a blue light as occurs with the unreduced co-created form, but instead give a broad spectrum of white visible light, when stimulated with UV LEDs in the range 350-405nm. This is a significant difference from what would have been expected, since it means that the mixture is emitting, more strongly, wavelengths that it either had previously emitted weakly or not at all.

That this effect is a cooperative effect, and is not due to a new phase, can be seen from the materials analysis of the systems and from the fact that the similar system with two similar components, $\text{Ba}_{12.25}\text{Al}_{21.5}\text{Si}_{11.5}\text{O}_{66}$ / $\text{BaAl}_2\text{Si}_2\text{O}_8$ / BaAl_2O_4 with particular proportions also gives a blue-white light with a broad spectral peak, when stimulated with UV LED light in the range 350-405nm, but in this case the choice of the LED used is critical, the brighter sources giving the better results, showing that a threshold stimulation may be needed for at least one component (use of weaker LEDs results in a violet light, and as noted above other compositions of the same mixture give a blue light).

Fig. 1 shows the emission spectrum on 330 nanometer excitation for a phase mixture of above mentioned $\text{Ba}_{12.25}\text{Al}_{21.5}\text{Si}_{11.5}\text{O}_{66}$ / $\text{BaAl}_2\text{Si}_2\text{O}_8$ / BaAl_2O_4 . The response is white as can be seen from the broad peak in the visible wavelength, which is clearly different to the luminescence as a sum of the luminescence of the individual compounds. The spectrum shows the intensity in relative strength (y-axis) against the wavelength in nanometer (x-axis).

Similarly the system SrAl_2O_4 / Sr_2SiO_4 , which contains none of the above constituents, gives white light under the brighter and longer wavelength UV LED stimulation in the range 350-405nm. Fig. 2 shows the spectrum of said system with its intensity in relative strength (y-axis) against the wavelength in nanometer (x-axis).

Mixtures of BaAl_2O_4 / SrAl_2O_4 across the 0-100% composition range show that between 90% and 70% BaAl_2O_4 the emission color can be noticeably shifted from the normal gold of both systems individually towards higher wavelengths, with orange emission at the 50/50 proportions.

It is clear that this effect arises through the non-independent i.e., co-operative behavior of the materials involved, where this co-operation is importantly occurring on the radiation-emission level, but, so far as can be determined, NOT on the chemical level. To be exact, the mixture, suitably analyzed to the best available ability, can be shown to remain a simple mixture, i.e., chemical reaction between the mixture components to create a new physical material not originally present, to which the unusual radiation emission might plausibly be ascribed, has not taken place, so far as it is determinable.

The phase $\text{Ba}_{12.25}\text{Al}_{21.5}\text{Si}_{11.5}\text{O}_{66}$, an important part of at least two of the three-component mixtures noted above, is a new specific phase and is duly claimed as such.

The observations are recent, and so the exact nature of this novel cooperative interaction is still the subject of theory and academic debate, but its exact nature does not prevent or pre-terminate this disclosure.

This disclosure thus claims all cases for the emission of electromagnetic radiation from mixtures of two or more materials subject to stimuli where the spectral emission is not calculable at a first approximation as the simple weighted sum of the spectral emissions of the materials independently subject to said stimuli.

A device for use of these materials can be a device comprising three individual luminescent materials, each of these three emitting within a different primary color wavelength, but preferably being pumped with one specific wavelength. It will then be possible to use e.g. a laser directed on said three materials to induce the full color response. Such a device can be described as a solid 3D display, if a laser diode is used.

Experimental Results

This report comprises a summary of compounds synthesized for fast and intense phosphors with high quantum yield. Compounds are mainly made of a host lattice (oxides, silicates, borates and halides including alkaline earth elements as Ca, Sr, Ba with doping / co-doping a rare earth element (Eu, Ho,...) in a polar crystallographic environment. They may also be mixtures of luminescent samples or solid solutions to modify the host lattice. As a function of the matrix and the co-dopants, the phosphor

colors vary from red to clear white.

The equipment comprises the following solid state synthesis equipment: several LT furnaces 1000°C, HT furnace 1600°C, H₂ / N₂ furnace up to 1100°C, Xray diffractometer (powder - single crystal) and refinement software (TOPAS, Rietveld), Spectrometer, UV-LED system, Quant. intensity measurement device, UV lamp 2 wavelengths, Commercial Black lamp, Low tech UV "money tester".

Short description of the general procedure:

First step: Synthesis is made mainly by ceramic methods from reagent grade pure oxides / halides or precursors in adequate crucibles (corundum, platin, graphite), followed by X-ray diffraction phase analysis and preliminary UV inspection.

Control of phases and crystal size leads to the Second step: Optimization and adjustment of the synthesis.

Third step: Reduction of Eu(III) (if EU(III) was used) in a N₂/H₂ furnace followed by Xray analysis and UV inspection. Spectrometric analysis

In some cases different synthesis and analysis methods were used and will be explained when necessary.

The following systems were used.

Silicates and mixed silicates: XAl_2SiO_8 (X= Ba, Sr), $XSiO_3$ (X = Ca, Sr, Ba), X_2SiO_4 (X = Ca, Sr, Ba), $Ba_{12.25}Al_{21.5}Si_{11.5}O_{66}$, $Sr_3Al_{10}SiO_{20}$, $SrAl_2SiO_7$.

Aluminates : $SrAl_{12}O_{19}$, XAl_2O_4 (X= Sr, Ba).

Fluorides : $BaMgF_4$, $SrMgF_4$, $Ba_6Mg_7F_{26}$, $Ba_{12}F_{19}Cl_5$, $Ba_7F_{12}Cl_2$.

Borates : $Ba_2Zn(BO_3)_2$, $Ba_2Mg(BO_3)_2$.

Silicates:

Alkaline earth ortho-silicates such as Ca_2SiO_4 , Sr_2SiO_4 and Ba_2SiO_4 are promising host lattices for doping with rare earth metal ions to obtain phosphor materials. To understand the influence of various parameters on the luminescence intensity of $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ the following parameters were chosen:

Doping with the fluoride or oxide of the rare earth (F or O)

Dopant concentration (0.5 or 2.5 mol%)

Calcination temperature (700°C or 900°C)

Reduction temperature (900°C or 1100°C)

Fig. 4 shows three X-ray diffraction spectra for Ca_2SiO_4 , one measured spectrum 41 being almost identical to a simulated spectrum and the difference spectrum 43. The luminescence of this system containing 100% Ca_2SiO_4 shows a very bright light blue luminescence with a high quantum output.

Fig. 5 shows three X-ray diffraction spectra for $\text{Ba}_{12.25}\text{Al}_{20.5}\text{Si}_{11.5}\text{O}_{66}$, one measured spectrum 51, one simulated spectrum 52 and the difference spectrum 53. The luminescence of this system containing 18.01% BaAl_2O_4 , 11,33% Hexacelsian and 70.68 $\text{Ba}_{12.25}\text{Al}_{20.5}\text{Si}_{11.5}\text{O}_{66}$ shows a very bright light yellow luminescence.

Fig. 6 shows three X-ray diffraction spectra for Ba_2SiO_4 , one measured spectrum 61 being almost identical to a simulated spectrum and the difference spectrum 63. The luminescence of this system containing 100% Ba_2SiO_4 shows a very intensive green luminescence with a high quantum output.

Fig. 7 shows three X-ray diffraction spectra for Sr_2SiO_4 , one measured spectrum 71 being very similar to a simulated spectrum 72 and the difference spectrum 73. The luminescence of this sys-

tem containing 100% Sr_2SiO_4 shows a blue-green luminescence with a good quantum output.

Luminescent Strontium Aluminum Silicates:

Within the work on the Sr-Al-Silicates, the initially as $\text{Sr}_6\text{Al}_{18}\text{Si}_2\text{O}_{37}$ suspected compound is now due to single crystal measurements proven to be $\text{Sr}_3\text{Al}_{10}\text{SiO}_{20}$, a new compound. Doped with EuF_3 it shows a very pale greenish luminescence after excitation. Probably this compound was not pure, there was always a small amount of SrAl_2O_4 (about 5 weight%) or $\text{SrAl}_{12}\text{O}_{19}$. Due to this there is no certainty about the luminescent properties of the pure phase although in one case the X-Ray analysis showed absence of SrAl_2O_4 and instead $\text{SrAl}_{12}\text{O}_{19}$ which is already known as strong phosphor with greenish luminescence. This sample showed blue fluorescence in both wavelengths (254 and 366nm) and yellowish-white phosphorescence. A remarkable phase is a sample containing Sr-Gehlenite ($\text{Sr}_2\text{Al}_2\text{SiO}_7$) doped with EuF_3 . Although in this sample again we were not able to remove the small amount of SrAl_2O_4 (about 5%) the strong bright luminescence can not be only due to this small amount of byphase. To complete the work on the Sr-Al-Silicates the compounds were doped with the rare earth oxides to compare luminescent properties to the doping with fluorides. In all cases the doping with oxides gives weaker luminescent properties. The following Table shows the researched compounds.

Strontium Aluminum Silicates:

Assay No.	System	Dopant	Color			Phosphorescence	
			Vis	254nm	366nm	Color	Intens.
38a	$\text{Sr}_2\text{Al}_2\text{SiO}_7$	Eu^{2+}	White	orange, yellow spots	green	pale blue	v. strong
38b	$\text{SrAl}_2\text{O}_4, \text{Al}_2\text{O}_3$	Eu^{2+}	White	white	white	greenish	strong

						white	
40	$\text{SrAl}_2\text{Si}_2\text{O}_8$	Eu_2O_3	White	darkred	abs., white spots	yellow	weak
42	$\text{Sr}_3\text{Al}_{10}\text{SiO}_{20}$	Eu^{2+}	White	yellow	yellow	greenish	weak

*Intensity: v. weak < weak < strong < v. strong,

Luminescent Earthalkali and Earthalkali/Zinc Silicates:

The investigations on Silicates were broadened on the system of earth alkali and earth alkali/zinc silicates. Due to reports in literature of luminescent properties of Akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$ doped with Eu_2O_3) and Mervinite ($\text{Ca}_3\text{MgSi}_2\text{O}_8$ doped with Eu_2O_3) the different Earthalkali analogue of these compounds are the aim of new syntheses. This field of silicate compounds offers a large number of different possible matrices for luminescent materials. According to the structures of Akermanite and Mervinite two more systems are under found based on Orthosilicates CaMgSiO_4 and $\text{CaMgSi}_2\text{O}_6$. A short overview over the new field of compounds can be given as follows:

1	XYSiO_4	X = Ba, Sr, Ca Y = Mg, Zn
2	XYSi_2O_6	
3	$\text{X}_2\text{YSi}_2\text{O}_8$	
4	X_3YSiO_7	
5	$\text{X}_3\text{YSi}_4\text{O}_{12}$	

As a first step compositions 1 and 2 were screened. Substitution of Ca with Ba and Sr were tried, as well as substitution of Mg with Zn. X-Ray analysis showed that only a few of the expected phases were obtained by synthesis. The most common byproduct are the mervinites and akermanites analogue of the different earthalkalisilicates. Although luminescence properties of these two phases are mentioned in literature mostly these reports deal

with doping by oxides while our compounds achieve luminescence with fluorides. And as an effect of different byproducts of the reaction the mixtures show different luminescent properties as pure phases. Some of these systems contained of up to three different phases, doping with EuF_3 showed in all cases fluorescent properties in different colors and in more than 50% of the mixtures strong phosphoresces properties in greenish to nearly white colors. The most remarkable assay of the first screening step is a composition of SrSiO_3 (8,3%), $\text{Sr}_3\text{MgSi}_2\text{O}_8$ (11,7%) , $\text{Sr}_2\text{MgSi}_2\text{O}_7$ (39,1%) and a large amount of unreacted Quartz (40,7%). This sample showed very bright pale blue phosphorescence although it is only doped with EuF_3 without any codopant. In assay number 30 a new phase was found of the assumed composition $\text{Ca}_3\text{ZnSi}_2\text{O}_8$.

Procedure for XYSiO_4 :

A stoichiometric mixture of SrCO_3 , BaCO_3 or CaCO_3 and SiO_2 was slowly heated to 1250°C in a Al_2O_3 crucible. The reaction was kept at temperature 12h and cooled to room temperature within 6 hours. In a reductive atmosphere in pure H_2 gas flow the grinded powders are doped with 1-2% of EuF_3 .

Procedure for XYSi_2O_6 :

A stoichiometric mixture of SrCO_3 , BaCO_3 or CaCO_3 and SiO_2 was slowly heated to 1050°C in a Al_2O_3 crucible. The reaction was kept at temperature 12h and cooled to room temperature within 6 hours. In a reductive atmosphere in pure H_2 gas flow the grinded powders are doped with 1-2% of EuF_3 .

The obtained powders were analyzed with x-ray powder diffraction using a $\text{Cu K}_{\alpha 1,2}$ radiation source.

Assay 31 has the most interesting luminescent properties:

Assay No.	System	Dopant	Color			Phosphorescence	
			vis	254nm	366nm	Color	Int
28	$\text{Sr}_3\text{MgSi}_2\text{O}_8$, $\text{Sr}_2\text{MgSi}_2\text{O}_7$, MgO	Eu^{2+}	white	orange	absorbing	greenish	strong
30	$\text{Ca}_2\text{ZnSi}_2\text{O}_7$, Zn_2SiO_4 , ZnO , $\text{Ca}_3\text{ZnSi}_2\text{O}_8$ (?)	Eu^{2+}	white	Grey	grey	pale yellow	weak
31	SrSiO_3 , $\text{Sr}_3\text{MgSi}_2\text{O}_8$, $\text{Sr}_2\text{MgSi}_2\text{O}_7$, SiO_2	Eu^{2+}	white	pale pink	blue	pale blue - white	v. strong
32	BaSiO_3 , BaMgSiO_4 , SiO_2 , MgO	Eu^{2+}	white	Pink	pale blue	greenish	strong
34°	BaSiO_3 , BaZnSiO_4 , SiO_2 , ZnO	Eu^{2+}	white	greenish yellow	yellow	green	strong
34b	BaSiO_3 , BaZnSiO_4 , SiO_2 , ZnO	Eu^{2+}	white	green	yellow	green	strong

*Intensity: v. weak < weak < strong < v. strong,

$\text{Ba}_{13}\text{Al}_{22}\text{Si}_{10}\text{O}_{66}$ and new orthosilicates

As a result of the investigations on Sr-Aluminosilicates and the screening processes the focus was switched to the Ba-Aluminosilicates. Previous studies showed that the emission lines of Ba compounds are broadened in relation to the Sr compounds. Nevertheless we are still looking on Sr and Ca compounds.

The work is splitted up into two major fields, first, further screening on a lot of different compounds in the rare earth doped Alkali-Aluminosilicates as can be seen in the following table, second, to focus now on one promising phase like the system of $\text{Ba}_{13}\text{Al}_{22}\text{Si}_{10}\text{O}_{66}$ and it's related phases and byphases. Furthermore we revert to the latest results on $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ and solid solutions.

Fig. 3 shows three X-ray diffraction spectra for $\text{Ba}_{13.3}\text{Al}_{30}\text{Si}_6\text{O}_{70}$,

one measured spectrum 31, one simulated spectrum 32 and the difference spectrum 33. The luminescence of this system containing 83.54% BA20, 9.88% BaAl₂O₄ and 6.79% Hexacelsian shows a very bright luminescence.

Results on Ca₂ZnSi₂O₇ and solid solutions and modifications:

The screening of the Manganese and Zinc compounds is finished. The theoretically assumed phases were not stable at our conditions, only the Ca₃ZnSi₂O₈ could be isolated as a new phase but did not show any remarkable new luminescent properties. The syntheses of all other samples produced only mixtures from different oxides, which were already well known by literature, like Mervinite and Akermanite.

2.3. Latest results on Sr-Aluminumsilicates

To complete our investigations on Sr₃Al₁₀SiO₂₀ we tried to replace Sr with Ba and Ca to rise the phosphorescence duration and intensity. According to the size of the Ba²⁺ ion it was not astonishing that the doping did not work. The small distance between the Sr²⁺ and O²⁻ ions induce a huge stress in this structure, which agrees with the difficult synthesis. Due to this stress in structure the Ba ion would not replace the smaller Sr ion. The much smaller Ca²⁺ ion seems to replace the Sr ion in a small percentage. This can be seen in the reduction of the lattice parameter a from 15,15 to 15,08Å. Doping with Europium and reduction with Hydrogen showed a weak increase of luminescence intensity, the color is almost the same.

Screening of other compounds:

During the work on the Ba compounds, other phases are still screened. After closing the field of the Manganese and Zinc systems research was started on other Earthalkaline-Aluminumsilicates, previously found as byphases in the Sr-

Aluminosilicate synthesis. These compounds are XSiO_3 and X_3SiO_5 with $\text{X} = \text{Ca}, \text{Ba}, \text{Sr}$. In a first step we tried to get pure phases and dope them with Eu^{2+} in a second step. As far as results of these experiments are available, they are listed in the table below.

Procedure:

The ground powders of carbonates and oxides are heated up to 1200° within 5 h and kept at this temperature for 14 h. To get the pure phases the grinding and heating has to be repeated twice. Doping is done with EuF_3 before the first heat treatment.

	Color of UV excitation and phosphorescence					
	$\text{XSiO}_3:\text{Eu}^{3+}$			$\text{X}_3\text{SiO}_5:\text{Eu}^{3+}$		
X =	Ba	Ca	Sr	Ba	Ca	Sr
254 [nm]	red	red	red	dark red	blue	bright red
366 [nm]	dark red , green spots	red	red	dark red	dark red	absorb- ing
Phosphores- cence	-	-	-	red, strong	-	weak

$\text{Ba}_{13}\text{Al}_{22}\text{Si}_{10}\text{O}_{66}$:

This is one of the most promising systems of the work. This phase was found as a by product on the synthesis of an assumed composition of $\text{BaAl}_2\text{SiO}_6$ which is not a stable phase in the Ba-Aluminosilicate system. Other byphases were BaAl_2O_4 already known as a bright greenish phosphor and $\text{BaAl}_2\text{Si}_2\text{O}_8$ (Hexacelsian) known as a weaker blue phosphor. The luminescence of this system containing 33% $\text{BaAl}_2\text{SiO}_6$, 25% BaAl_2O_4 and 42% $\text{BaAl}_2\text{Si}_2\text{O}_8$ shows a very bright white luminescence at 254 and 366 nm and a strong phosphorescence with a very pale blueish color. As we know that the Bariumaluminate is related to the Luminova compound we will try

as a next step to replace the Aluminum with Silicate and combine it with the BA13 and the Hexacelsian. Due to earlier investigations on orthosilicates the inventors know that the Ba_2SiO_4 has similar color and intensity properties as the BaAl_2O_4 . Astonishing is that the single phases show a greenish to blueish fluorescence color while an in situ synthesized mixture of all three phases is white in fluorescence. It is assumed that this effect is due to a mixture of red, green and blue emission similar to the RGB color system. Why this effect is only observed in a in situ synthesis and reduction step and not in a mixture of the pure phases is not yet clear.

A higher calcination temperature gives a higher luminescence intensity of $\text{Ba}_2\text{SiO}_4: \text{Eu}^{2+}$ for both fluoride and oxide dopants. For fluorine dopants in $\text{Ba}_2\text{SiO}_4: \text{Eu}^{2+}$ at low calcination temperatures a higher dopant concentration leads to a higher intensity while at 900°C a higher dopant concentration diminishes the intensity. For oxygen dopants in $\text{Ba}_2\text{SiO}_4: \text{Eu}^{2+}$ at low calcination temperatures a higher dopant concentration leads to a lower intensity while at 900°C a higher dopant concentration raises the intensity.

The temperature of calcination has no influence on the specific surface area of calcined $\text{Ba}_2\text{SiO}_4: \text{Eu}^{2+}$ powders. The concentration of the dopant as well as the introduction of fluorine cause a lower specific surface area and therefore bigger particle sizes of the powder.

An attempt was made to synthesize new strontium aluminum oxide fluorides. The reactions yielded the well known compounds $\text{Sr}_3\text{AlO}_4\text{F}$ and $\text{Sr}_6\text{Al}_{12}\text{O}_{32}\text{F}_2$. The luminescence properties of these samples doped with EuF_3 were studied. $\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}\text{Cl}_2$ was doped with Eu^{3+} , Pr^{3+} and its luminescence behavior was investigated. Com-

pounds with the composition $M(II)M(III)_2O_4$ with $M(II) = Mg, Sr$ and $M(III) = Y, Ga$ were doped with rare earth metals. The luminescence of these compounds was also observed under exposure to UV light. A sodalite, $Ca_8(Al_{12}O_{24})(WO_4)_2$ doped with EuF_3 was studied as well.

Sr_3AlO_4F and $Sr_6Al_{12}O_{32}F_2 : Eu^{3+}$

Mixtures of $SrCO_3$, SrF_2 and $Al(NO_3)_3 \cdot 9H_2O$ with 0.5 mol% EuF_3 were ground, pressed and placed in a corundum crucible. The crucible was kept at $100^\circ C$ for 24h to release water. Then it was heated to $700^\circ C$. It was kept at that temperature for 24 hours, another 24 hours at $800^\circ C$ and another 24 hours at $900^\circ C$. The mixture was reground and fired at $1050^\circ C$ for 72 hours. The samples were reduced in a tube furnace under pure H_2 for 2h at $1000^\circ C$

$Ca_{12}Al_{14}O_{32}Cl_2 :$

A stoichiometric mixture of $CaCO_3$, $Al(OH)_3$ and $CaCl_2 \cdot 3H_2O$ was doped with 0.5mol% of LnF_3 with $Ln = Eu$ or Pr was ground, pressed and placed in a platinum crucible. Then it was heated to $1000^\circ C$ and kept at that temperature for 1 hour.

$Ca_8(Al_{12}O_{24})(WO_4)_2 :$

A stoichiometric mixture of $CaCO_3$, $Al(OH)_3$ and WO_3 with 0.5 mol% EuF_3 and 0.5 mol% DyF_3 was heated to $1200^\circ C$ and kept at this temperature over night. The product was ground, pressed and fired again at $1300^\circ C$. Eu^{3+} was reduced in a tube furnace under pure H_2 for 2h at $1000^\circ C$.

$SrY_2O_4 :$

A stoichiometric mixture of $SrCO_3$ and Y_2O_3 was ground, pressed and heated to $1550^\circ C$ in a corundum crucible and kept at that temperature for 72 hours. For doping the product was mixed with the rare earth fluoride and heated in a tube furnace under pure H_2 to $1000^\circ C$. The reaction mixture was kept at this temperature

for 2 hours.

SrGa₂O₄:

A stoichiometric mixture of SrCO₃ and Ga₂O₃ was ground, pressed and heated to 1200°C in a corundum crucible and kept at that temperature for 72 hours. For doping the product was mixed with EuF₃ and heated in a tube furnace under pure H₂ to 1000°C. The reaction mixture was kept at this temperature for 2 hours.

MgGa₂O₄:

A stoichiometric mixture of MgCO₃ and Ga₂O₃ was ground, pressed and fired at 1000°C in a corundum crucible for 6 hours.

Sr₃AlO₄F and Sr₆Al₁₂O₃₂F₂ : Eu³⁺

Assay No.	Substance	Dopant	Uv-Luminescence
Sra I	Sr ₃ AlO ₄ F	Eu ³⁺	red orange at 254 and 366 nm
Sra II	Sr ₆ Al ₁₂ O ₃₂ F ₂	Eu ³⁺	weak red at 366nm , red at 254nm

Ca₁₂Al₁₄O₃₂Cl₂:

Assay No	Substance	Dopant	Uv-Luminescence
Ca I	Ca ₁₂ Al ₁₄ O ₃₂ Cl ₂	Eu ³⁺	red at 254nm
Ca III	Ca ₁₂ Al ₁₄ O ₃₂ Cl ₂	Eu ²⁺ /Pr ³⁺	red at 254nm*

* the red color shows that it was not possible to reduce most of the Eu³⁺ in this compound

Ca₈(Al₁₂O₂₄)(WO₄)₂:

Assay No.	Substance	Dopant	Uv-Luminescence
W I	Ca ₈ (Al ₁₂ O ₂₄)(WO ₄) ₂	Eu ³⁺	dark orange at 254nm
W II	Ca ₈ (Al ₁₂ O ₂₄)(WO ₄) ₂	Eu ²⁺	dark orange at 254nm

SrY₂O₄:

Assay No.	Substance	Dopant	Uv-Luminescence
SrY I	SrY ₂ O ₃	Eu ³⁺	intensive red at 254nm

SrY II	SrY_2O_3	Eu^{2+}	intensive red at 254nm
SrY III	SrY_2O_3	Mn^{2+}	dark red
SrY IV	SrY_2O_3	$\text{Ho}^{3+}, \text{Mn}^{2+}$	dark red
SrY V	SrY_2O_3	Tb^{3+}	yellow with
SrY VI	SrY_2O_3	Ce^{3+}	Absorbing

SrGa₂O₄:

Assay No.	Substance	Dopant	Uv-Luminescence
SrG I	SrGa_2O_3	Eu^{3+}	red at 254nm
SRG III	SrGa_2O_3	$\text{Ho}^{3+}, \text{Mn}^{2+}$	absorbing

MgGa₂O₄:

Assay No.	Substance	Dopant	Uv-Luminescence
Mg I	MgGa_2O_3		green at 254nm

Sr₃AlO₄F and Sr₆Al₁₂O₃₂F₂ : Eu³⁺

Several attempts were made to synthesize new strontium aluminum oxide fluorides. The products always contained $\text{Sr}_3\text{AlO}_4\text{F}$ and $\text{Sr}_6\text{Al}_{12}\text{O}_{32}\text{F}_2$ and several strontium aluminates, e.g. SrAl_2O_4 . The samples showed red luminescence before the reduction and some showed pale blue/white luminescence after the reduction. In some samples the red colour was not affected by the treatment with pure H_2 .

Ca₁₂Al₁₄O₃₂Cl₂:

$\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}\text{Cl}_2$ showed red luminescence when it was doped or co-doped with Eu^{3+} .

Ca₈(Al₁₂O₂₄)(WO₄)₂ : Eu

The samples showed orange luminescence under UV light at 254nm but no after-glow.

SrY₂O₄:

SrY₂O₄ showed weak after-glow when it was doped with Eu²⁺ and with Tb³⁺.

SrGa₂O₄:

The typical Eu²⁺ luminescence was not observed.

Borates (Eu), Studies on luminescent ortho- and metaborates:

Mixed borates of barium and another alkaline earth metal or zinc were synthesized and doped with rare earth metals such as europium and ytterbium. Some of the resulting powders were reduced in a tube furnace under N₂/H₂ atmosphere. The luminescence of the products was investigated using UV light with a wavelength of 254 and 366nm.

Stoichiometric quantities of BaCO₃ and H₃BO₃ were mixed with either MgO, CaCO₃ or ZnO and 0.5 mol % of a rare earth fluoride (rare earth = Eu, Yb) and pressed to a pellet.

All syntheses were carried out in platinum crucibles. In a first step the crucibles were heated to 800°C within 8 hours and kept at that temperature for 12 hours. After cooling the mixture was reground and pressed again. In a second firing step they were heated to 850°C and kept at that temperature for 12 hours.

Ba₂Zn(BO₃)₂ was doped with Mn²⁺, Sm³⁺ and Eu³⁺ in a tube furnace at 800°C. For that purpose the tube furnace was purged with pure H₂. Ba₂Mg(BO₃)₂ : Eu³⁺ was reduced under the same conditions.

say No.	Substance	Dopant	Uv-Luminescence
Ia	Ba ₂ Zn(BO ₃) ₂	Eu ³⁺	weak red at 366nm, intensive bright red at 254nm
Ib	Ba ₂ Zn(BO ₃) ₂	Eu ³⁺ ; Eu ²⁺	orange at 254nm

B Ic	Ba ₂ Zn(BO ₃) ₂	Sm ³⁺	bright orange at 254nm
B Id	Ba ₂ Zn(BO ₃) ₂	Mn ²⁺	Absorbing
B Ii	BaZn ₂ (BO ₃) ₂	Eu ³⁺	weak red at 254nm
B IIIa	Ba ₂ Mg(BO ₃) ₂	Eu ³⁺	red at 366nm; intensive orange at 254nm; red x-ray luminescence
B IIIred	Ba ₂ Mg(BO ₃) ₂	Eu ³⁺ ; Eu ²⁺	intensive orange at 366 and 254nm
B IV	Mg ₂ B ₂ O ₅ ; Ca ₂ B ₂ O ₅ Ca(BO ₂) ₂	Eu ³⁺	orange at 254nm; red x-ray luminescence
B Va	BaZn ₂ (BO ₃) ₂	Tb ³⁺	yellow at 254nm
B Vb	BaZn ₂ (BO ₃) ₂	Sm ³⁺	orange at 254nm
B Vc	BaZn ₂ (BO ₃) ₂	Bi ³⁺	Absorbing
B VI	Ba ₂ Mg(B ₃ O ₆) ₂	Tb ³⁺	yellow greens
B VII	Ba ₂ Ca(B ₃ O ₆) ₂	Tb ³⁺	yellow green
B VIII	Ba ₂ Zn(B ₃ O ₆) ₂	Eu ³⁺	red at 254nm
B IX	Ba ₂ Ca(BO ₃) ₂	Eu ³⁺	orange at 254nm

The invention is based on the insight that, when talking about combinations of halides and oxides, the choice of host and dopant is not symmetrical: in short, that doping oxides into fluorides is not the same as doping fluorides into oxides. The reason is the insight that the dopant-fluoride pair travel AS A PAIR into the matrix, and hence the dopant rare-earth ion nearly always ends up in non-symmetric surroundings, which is vital for luminescence. Hence, this tends to lead to more effective - and hence efficient - materials.

Additionally further compounds have been found to exhibit luminescence according to the above mentioned principles. These are discussed and described as follows.

SrAl₂Si₂O₈ [Eu(II)] - a blue phosphor

Bluish phosphors have been found in the past years by different research groups. One of these materials is SrAl₂Si₂O₈ (SAS),

doped with Eu_2O_3 it emits weak blue luminescence. To improve color and intensity of this phosphor as a base for a new white light emitting material, a physical mixture of a yellow and a blue phosphor was prepared to show white fluorescence after excitation with nitrogen lamp. Improvement of the bluish SAS was done by doping it with rare earth (RE) fluorides and adding small amounts of boron acid or sodium fluoride as flux (supporting shorter reaction time) and to change color properties of the materials. Adding boron to the reaction improved synthesis time and gave all samples a pinkish touch. NaF addition had same influence on reaction progress than boron acid but shifted color of the doped samples to very pale blue - close to white - color.

An in situ prepared mixture of different silicates and aluminosilicates emits different colors than physical mixtures of the same materials creating a new intensive blue phosphor with different blue colors. While the pure phase shows weaker intensity and a slightly pink touch, the mixtures of SAS with some other silicates and aluminosilicates show more intensity or a brighter blue. Highest emission yield was obtained at 254nm excitation. The emission peak of the SAS has its highest intensity about 405 nm (see Fig. 8) in the blue region.

	Phase composition in %					fluorescence color
Sample	SAS	SrSiO_3	SrAl_2O_4	$\text{SrAl}_{12}\text{O}_{19}$	Educts	
AR006	100	-	-	-	-	blue
AR015	63	11	6	11	9	pale blue
K2	68	14	-	11	7	blue (strong)

Pure SAS powders were obtained from a well homogenized mixture of pro analytical SrCO_3 , $\text{Al}(\text{OH})_3$ and SiO_2 powders. The powders were pressed to pellets and fired at 1450°C for 8h with a heating rate of 200°C/h. RE doping with EuF_3 or other RE fluorides

was done at 1000°C for 2h. XRD measurements show pure SAS phase without by products (Fig. 9).

Mixtures containing mainly SAS and other silicates or aluminosilicates, as shown in the table above, were obtained with the same educts fired at 1200°C for 10h. Doping was done at same conditions as above.

Sr₂SiO₄ - [Eu(II),La(III)] - a yellow phosphor

Stoichiometric amounts of pro analytical SrCO₃ and SiO₂, 0,5 mol% EuF₃ and 0,5 mol% LaF₃ were homogenized very well. The mixture was put into a mould and a pellet was formed at a pressure of 10 tons for 5 minutes. Thereafter the pellet was given into an aluminium oxide crucible and heated up to 1370°C for 12 hours with a heating rate of 200 °C/h. Alternatively the synthesis was done with Aerosil P300 instead of quartz at 850°C for 36 hours time, also with a heating rate of 200 °C/h.

Both syntheses showed the same results:

A phase mixture of orthorhombic and monoclinic Strontium silicate, where the ratio of the monoclinic phase was from 75% up to 98%.

The second step of preparation was the reduction of the RE. This was done at 1000°C for one and a half hour with a heating rate of 400 °C/h. The reduced powder was homogenized once more and analyzed by powder diffraction. The phase distribution was both times the same as before reduction.

Afterwards the luminescence properties of the powder were tested by irradiation under UV at 254 nm and 366 nm. The fluorescence was a bright light yellow.

Also the phosphorescence was yellow and could be seen by the naked eye for about an hour. The phosphorescence can be depressed by adding small amounts of boric acid or iron.

Fig. 10 shows the emission for this compound, named sample GW004. It can be seen that at 280nm there are two overlapping Eu bands (reference numeral 100). Excitation spectra measured at 440, 540 und 600 nm (i.e. 101, 102, 103) show, that at an excitation at 370 nm the second band is more intensive. The emission spectra at 370 nm confirm to this (sample GW 004; reference numeral 104).

With the two above mentioned intensive luminophores different physical mixtures were made. Mixing the yellow and the blue compound all color shades between yellow and blue were obtained. Although concerning the RGB system no red emitting material is in the mixture the obtained powders show bright white emission.

Fig. 11 shows an excitation spectrum of sample W1. The different lines 111, 112 and 113 show the excitation at 3 fixed emission wavelengths (402, 465 and 538 nm). Excitation spectra show three different broad peaks with a maximum excitation around 250 nm. These peaks can be determined as SAS excitation at 250nm and Sr_2SiO_4 excitation at 320 and 370nm. The Sr_2SiO_4 signal is split in two peaks presumable due to the alpha and beta phase.

Fig. 12 shows emission spectra of W1 at different wavelengths. Best results were obtained at 360nm (reference numeral 123) were all three peaks showing same intensity. The step in the line 121 is due to switching the filter in the spectrometer. Emission spectra 121 shows a very intense peak around 400nm under short wave irradiation with UV light at 254nm. The best emission profile 123 was obtained under 360nm were all peaks show the same

intensity.

These compounds show non-predictable colour effects upon mixing and are formed using halide dopants in the oxide matrix. They are new in the sense that some use two, not one, cationic dopants, of which one is Eu.

Finally, a new class of highly luminescent red-emitting fluorescent materials based on aluminates have been found, based on (a) 40% CaAl_4O_7 / 40% $\text{CaAl}_{12}\text{O}_{19}$ / 20% Al_2O_3 doped with Mn halides and (b) $\text{Li}_2\text{Al}_{10}\text{O}_{16}$ / LiAl_5O_8 doped with Fe (oxides, in this case, but halides also possible). Colour and luminescence vary with the amount of doping (and the wavelength of UV used to excite the materials) and furthermore, when mixed, the same mixing effects arise.

Red emitting phosphors based upon Al_2O_3 with Ca (with Mn doping) and Li (with Fe doping) have been mentioned by Virgil Mochel of the Corning Glass Works (J. Electrochem. Soc., April 1966, pp398-9) which describes $\text{Li}_2\text{O}_{0.5}\text{Al}_2\text{O}_3:\text{Fe}$ (thus compositionally equal to $\text{Li}_2\text{Al}_{10}\text{O}_{16}$, even though the actual phases may be different) and $\text{CaO}_{0.2}\text{Al}_2\text{O}_3:\text{MnCl}_2$ (thus equal to CaAl_4O_7 , ditto). However Mochel does not disclose (a) the additional phases beyond the first in each mixture (b) the particular phase mixtures - Mochel is in particular much richer in Al_2O_3 in the Ca-Mn system, and (c) the post-doping with halides.

Calcium aluminates doped with manganese

Starting from J. Electrochem. Soc. (1966), 113(4), 398-9 different mixtures of calcium aluminates doped with manganese were prepared.

				XRD results	Luminescence 254nm	366nm
AB129	400.4mg CaCO ₃	1248mg Al(OH) ₃	5mg MnCl ₂	95.12wt% CaAl ₄ O ₇ 4.88wt% CaAl ₂ O ₄	weak red	dark red
AB130	170mg CaO	830mg Al ₂ O ₃	0.5mg MnCl ₂	39.49wt% CaAl ₄ O ₇ 37.91wt% CaAl ₁₂ O ₁₉ 22.6wt% Al ₂ O ₃	dark red	strong red
AB131	400.4mg CaCO ₃	1248mg Al(OH) ₃	0.5mg MnCl ₂	94.42wt% CaAl ₄ O ₇ 6.58wt% CaAl ₁₂ O ₁₉	red with dark spots	dark red
AB132	224mg CaO	816mg Al ₂ O ₃	0.5mg MnCl ₂	61.3wt% CaAl ₄ O ₇ 19.35wt% CaAl ₁₂ O ₁₉ 19.35wt% Al ₂ O ₃	intensive red	strong red
AB133	84mg CaO	918mg Al ₂ O ₃	0.5mg MnCl ₂	9.85wt% CaAl ₄ O ₇ 38.06wt% CaAl ₁₂ O ₁₉ 52.1wt% Al ₂ O ₃	intensive red	strong red
AB135	224mg CaO	816mg Al ₂ O ₃	0.5mg MnF ₂	64wt% CaAl ₄ O ₇ 20.22wt% CaAl ₁₂ O ₁₉ 15.78wt% Al ₂ O ₃	intensive red	strong red

All powders were grinded, pressed to pellets and put into corundum crucibles. They were synthesized in air at 1370°C for 12h.

- 5 The following specimen were prepared of lithium aluminates doped with iron.

				XRD results	Luminescence 254nm	366nm
AB139	123.6mg Li ₂ CO ₃	950mg Al ₂ O ₃	1.3mg Fe ₂ O ₃	79wt% LiAl ₅ O ₈ 21wt% Al ₂ O ₃	intensive red	only weak luminescence
AB140	110.8mg Li ₂ CO ₃	764.7mg Al ₂ O ₃	1.0mg Fe ₂ O ₃	100% LiAl ₅ O ₈	intensive red	only weak luminescence

The preparation process was the same as for the calcium aluminates. The XRD results relate to Bruker AXS (2000), Topas V2.0, Karlsruhe, Germany.

Claims

1. An luminescent composition comprising a mixture of two or more materials, emitting electromagnetic radiation when subject to stimuli, wherein the spectral emission is not calculable at a first approximation as the simple weighted sum of the spectral emissions of the materials independently subject to said stimuli.
2. An luminescent composition comprising a mixture of two or more materials, emitting electromagnetic radiation when subject to stimuli, being a solid state material and/or material of essentially diffusionless character, of crystalline and/or amorphous and/or solid solution character(s), of ordered and/or disordered nature, and/or mixtures thereof, based on anionic matrices such as but not limited to oxides and/or fluorides and /or phosphates and/or sulphates and/or chlorides and/or mixed halides of alkaline cations, distinguished in that these matrices are altered by doping and/or co-doping with anionic salts of rare earth metals and/or alkaline metals where the choice of anion(s) in the anionic salt(s) is different from the anion(s) in the anionic host matrix.
3. The luminescent composition according to claim 2, further characterized in that the anionic matrix is an oxide and the doping anionic salt is a fluoride or vice versa.
4. The luminescent composition according to claim 2 or 3 which also contains a secondary cation not of the alkaline earth cations such as but not limited to those of Groups III and IV such as but not limited to Boron, Silicon and Aluminum so that the oxide matrix materials may be termed for instance borates, silicates, or aluminates, or mixed systems thereof.

5. The luminescent composition according to one of claims 2 to 4 irrespective of local, limited and/or general crystal modification to systems such as but not limited to different crystal classes, space groups, mixed systems, and/or any combination of the above.

6. The luminescent composition according to one of claims 2 to 5 in which the dopants are such as but not limited to europium (II) fluoride (EuF_2) and samarium fluoride (SmF_3), whether directly doped and/or arising from the preparation procedure such as but not limited to any reduction step, where the use of certain of these such as but not limited to SmF_3 is intended to create defects at the anion sites or traps on the cation site in the host matrix.

7. The luminescent composition according to one of claims 2 to 6, in which the cationic dopants are europium and none or more other elements.

8. The luminescent composition according to one of claims 2 to 6, in which the cationic dopants are alkaline, preferably sodium, lithium or potassium, and none or more other elements.

9. The luminescent composition according to one of claims 2 to 8, made by suitable solid state manufacturing techniques such as but not limited to precipitation, 'shake and bake' and sol gel.

10. The luminescent composition according to one of claims 1 to 9, wherein said stimuli are from a group comprising pressure, oscillating magnetic fields, introduction of damage, and further procedures to induce emission of electromagnetic radiation.

11. A method to induce emission of electromagnetic radiation from one of the materials as in claims 2-10 or from mixtures of two or more materials, where at least one material is a material as in claims 2-10 which are or have been subject to suitable stimuli where the emission may be predictive or non-predictive as for the composition according to claim 1.

12. The method according to claim 11, wherein said stimuli includes at least one stimulus comprising electromagnetic radiation or wherein said stimuli includes at least one stimulus comprising electromagnetic radiation falling in the ultra-violet part of the spectrum or wherein said stimuli includes at least one stimulus comprising electromagnetic radiation falling at least partly in the human-visible part of the electromagnetic spectrum.

13. The method according to claim 11, wherein said stimuli includes at least one stimulus comprising electrons or wherein said stimuli includes at least one stimulus comprising electrons supplied via direct electrical circuit or via indirect electron bombardment.

14. The method according to claim 11, wherein said stimuli includes at least one stimulus comprising ions.

15. A light emitting device providing emission of electromagnetic radiation from at least one of the materials of the luminescent composition according to claims 1 to 14.

16. The device according to claim 15, wherein the emitted electromagnetic radiation falls at least partly in the human-

visible part of the electromagnetic spectrum and/or wherein said stimuli include at least one stimulus comprising electromagnetic radiation, particularly falling in the ultra-violet part of the spectrum.

17. The device according to claim 15, wherein said stimuli includes at least one stimulus comprising electrons, particularly electrons supplied via direct electrical circuit or electrons supplied via indirect electron bombardment or said stimuli includes at least one stimulus comprising ions.

18. The device according to one of claims 15 to 17, wherein such device is a light/lamp bulb or a fluorescent light/lamp bulb or a light-emitting diode or a solid full color display.

19. The device according to one of claims 15 to 18, wherein the light emitting composition comprises a fluorescent paint or ink or colorant or dye or dyestuff.

20. The device according to one of claims 15 to 19, wherein the such device produces directly 'white light' either and/or by use of a mixture and/or an admixture of materials and/or by using filters and/or absorption and re-emission to achieve 'white light'.

21. A material for a luminescent composition according to one of claims 1 to 10, comprising SrAl_2O_4 , and/or doped with one or more rare earth elements preferably in the form of fluorides, especially as a bright white emitter, either alone or as part of a mixture or similar system.

22. A material for a luminescent composition according to one of claims 1 to 10, comprising and surrounding the compositions

$\text{Ba}_{12.25}\text{Al}_{21.5}\text{Si}_{11.5}\text{O}_{66}$ / $\text{Ba}_{13}\text{Al}_{22}\text{Si}_{10}\text{O}_{66}$, and/or doped with one or more rare earth elements preferably in the form of fluorides, and its use as a luminescent material, especially as a bright white emitter, either alone or preferably as part of a mixture or similar system.

23. The material according to claim 22, where the other components of the mixture are such as but not limited to $\text{Ba}_2\text{Si}_2\text{O}_8$, BaAl_2O_4 and/or $\text{BaAl}_2\text{Si}_2\text{O}_8$, wherein the mixture contains 1% - 99% $\text{Ba}_{12.25}\text{Al}_{21.5}\text{Si}_{11.5}\text{O}_{66}$, and 9-1% of all other components, individually and/or collectively.

24. A material for a luminescent composition according to one of claims 1 to 10, comprising $\text{Sr}_3\text{Al}_{10}\text{SiO}_{20}$ and/or doped with one or more rare earth elements preferably in the form of fluorides, either alone or as part of a mixture or similar system.

25. A material for a luminescent composition according to one of claims 1 to 10, comprising one or all systems of the strontium aluminum silicates, notably $\text{Sr}_2\text{Al}_2\text{SiO}_7$, $\text{SrAl}_2\text{Si}_2\text{O}_8$, and the phase $\text{Sr}_3\text{Al}_{10}\text{SiO}_{20}$ as in Claim 23, doped with Eu^{2+} in the form of fluorides.

26. A material for a luminescent composition according to one of claims 1 to 10, comprising $\text{Ca}_3\text{ZnSi}_2\text{O}_8$ and/or doped with one or more rare earth elements preferably in the form of fluorides, either alone or as part of a mixture or similar system.

27. A material for a luminescent composition according to one of claims 1 to 10, comprising one or all of the systems of the (alkali earth) / (magnesia / zincate) silicates, notably the phase as in Claim 22, doped with Eu^{2+} .

28. A material for a luminescent composition according to one of claims 1 to 10, comprising the simple alkaline earth simple halides, mixed alkaline earth simple halides, simple alkaline earth mixed halides, and mixed alkaline earth mixed halides, as doped with non-halide salts, preferably oxides, of rare earth elements such as but not limited to samarium and europium, and their use as luminescent materials.

29. The material according to claim 26, wherein the (alkaline earths)(halides) is the doped system, specifically the compositions of BaMgF_4 (doped Sm^{2+}) BaMgF_4 (doped Eu^{2+}) and $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ (doped Eu(II)) and alkalines.

30. The material according to claim 27, wherein the phase $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ (doped Eu(II)) as in Claim 24.

31. A material for a luminescent composition according to one of claims 1 to 10, comprising Sr_2SiO_4 and/or doped with one or more rare earth elements, preferably in the form of fluorides, either alone or as part of a mixture or similar system, and preferably doped with both EuF_3 and/or LaF_3 .

32. The use of boron acid and/or sodium fluoride as a flux during preparation of any of the materials in claims 21-31, and/or any variant material compositions resulting, according to claims 11-31.

33. A material for a luminescent composition according to one of claims 1 to 10, and/or as a material in its own right, comprising $\text{CaAl}_{12}\text{O}_{19}$, preferably doped with one or more transition metals, preferably Mn and/or Fe, preferably in the form of oxides and/or halides and/or doped with one or more rare earth elements preferably in the form of fluorides, either alone or as

part of a mixture or similar system, where this similar system may include CaAl_4O_7 and/or Al_2O_3 preferably doped with one or more transition metals, preferably Mn and/or Fe, preferably in the form of oxides and/or halides and/or doped with one or more rare earth elements preferably in the form of fluorides.

34. A material for a luminescent composition according to one of claims 1 to 10, and/or as a material in its own right, comprising a mixture of calcium aluminates, being based on 40% CaAl_4O_7 / 40% $\text{CaAl}_{12}\text{O}_{19}$ (as in claim 33) / 20% Al_2O_3 , all doped with Mn oxides and/or halides and/or doped with one or more rare earth elements, preferably in the form of fluorides, either alone or as part of a mixture or similar system, where this material composition by itself exhibits strong red luminescence.

35. A material for a luminescent composition according to one of claims 1 to 10, and/or as a material in its own right, comprising LiAl_5O_8 , preferably doped with one or more transition metals, preferably Mn and/or Fe, preferably in the form of oxides and/or halides and/or doped with one or more rare earth elements preferably in the form of fluorides, either alone or as part of a mixture or similar system, where this similar system may include $\text{Li}_2\text{Al}_{10}\text{O}_{16}$ preferably doped with one or more transition metals, preferably Mn and/or Fe, preferably in the form of oxides and/or halides and/or doped with one or more rare earth elements preferably in the form of fluorides.

36. A material for a luminescent composition according to one of claims 1 to 10, and/or as a material in its own right, comprising a mixture of lithium aluminates, being based on $\text{Li}_2\text{Al}_{10}\text{O}_{16}$ / LiAl_5O_8 (as in claim 35), both doped with Fe oxides and/or halides and/or doped with one or more rare earth elements preferably in the form of fluorides, either alone or as part of

a mixture or similar system, where this material composition by itself exhibits strong red luminescence.

37. A light source of electromagnetic radiation, especially visible colored radiation, more especially white radiation, wherein a blue/UV source such as but not limited to a blue/UV emitting light-emitting diode (LED) is combined with suitable luminescent material(s) and, optionally, other light absorbing materials such as coloured coatings.

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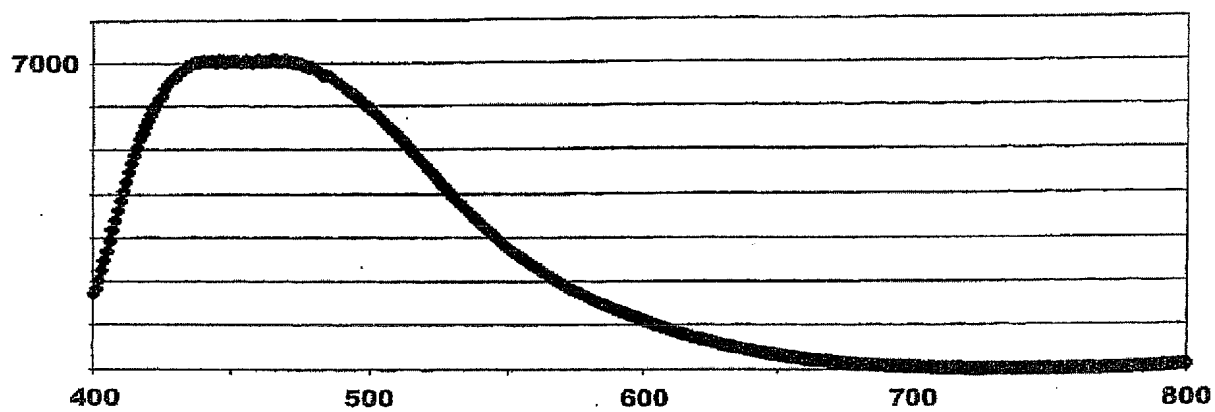


FIG. 1

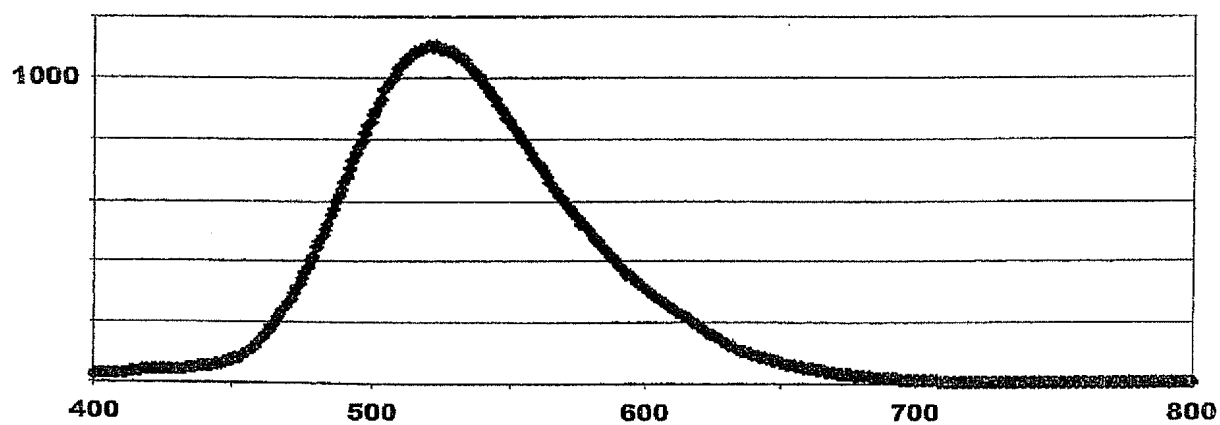
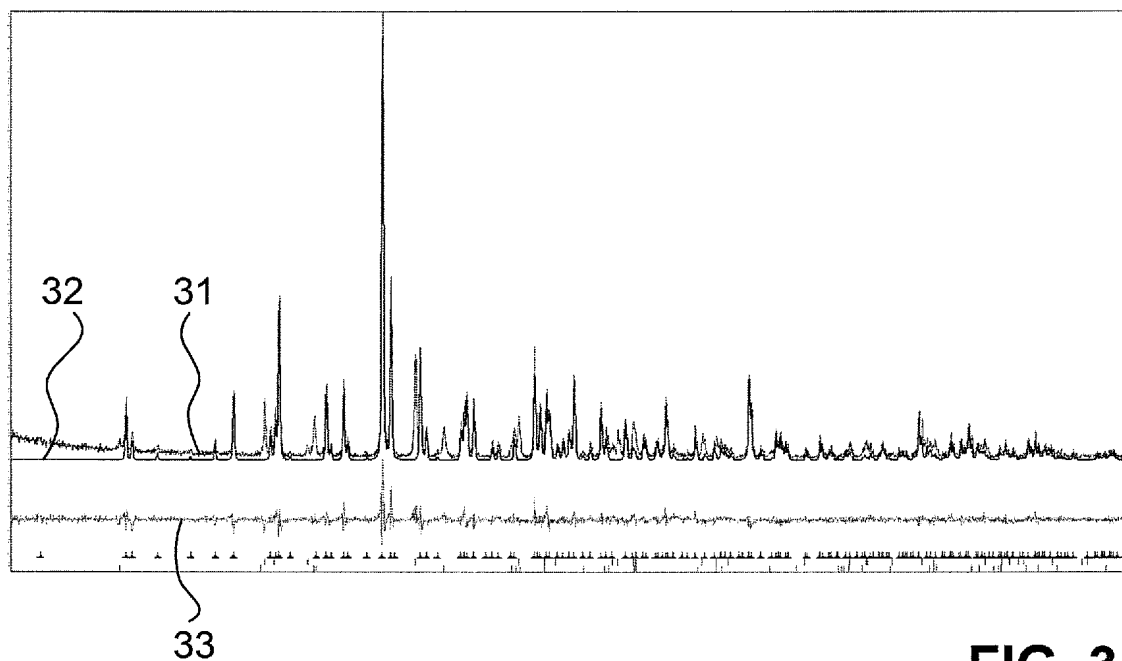
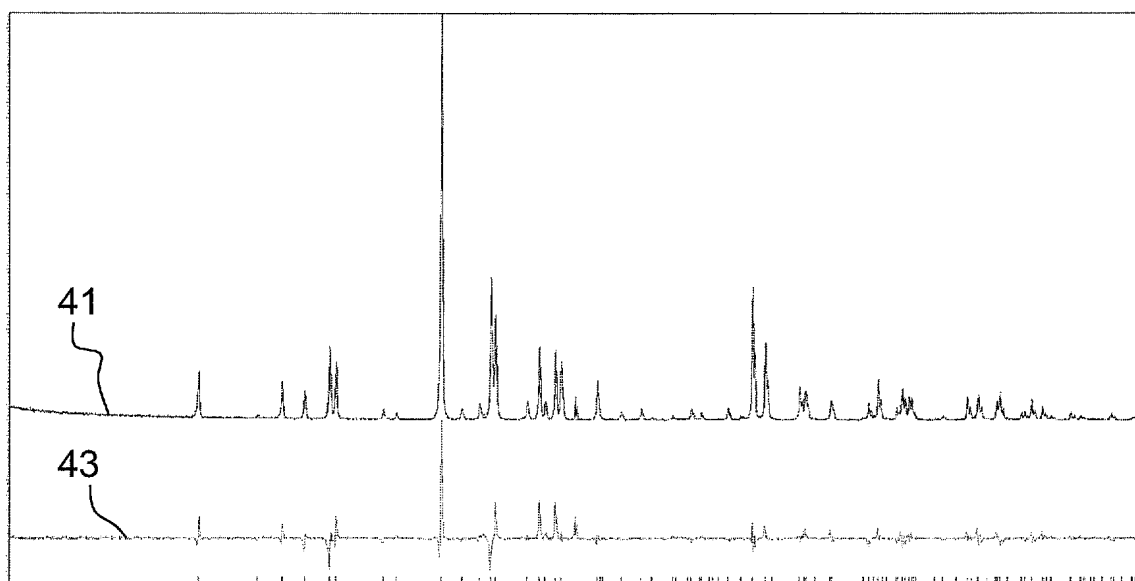
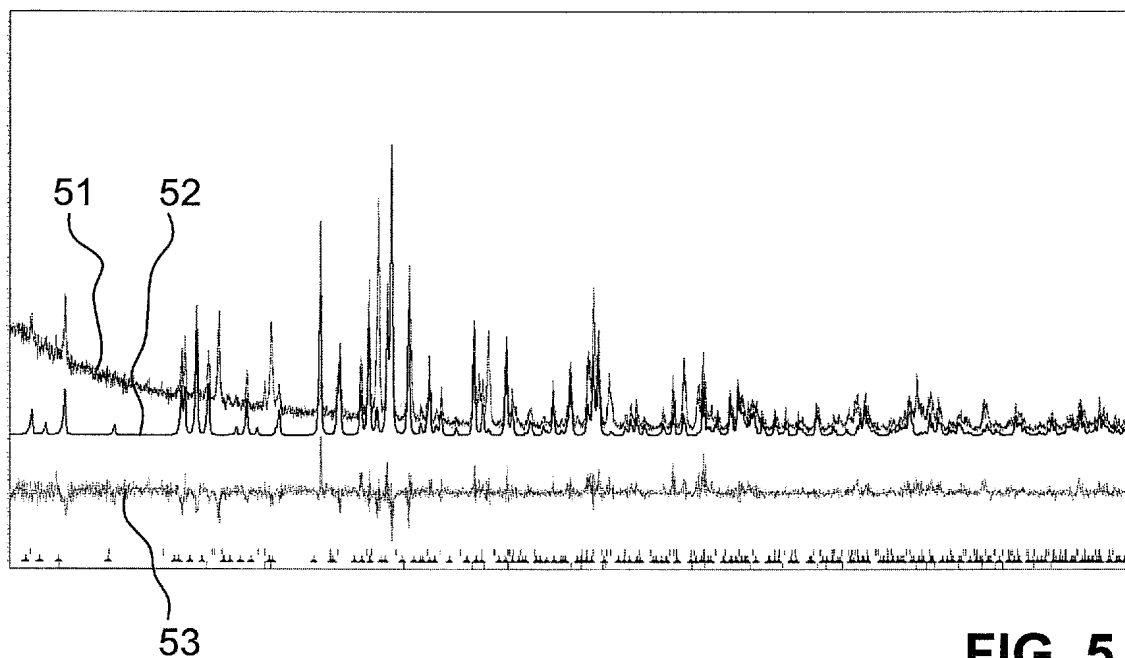
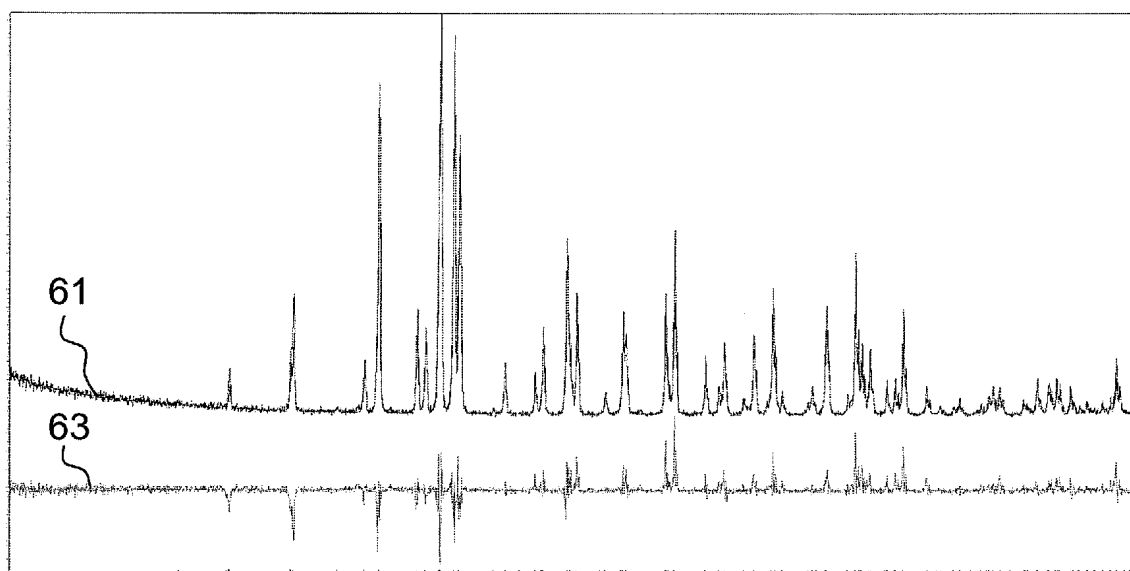


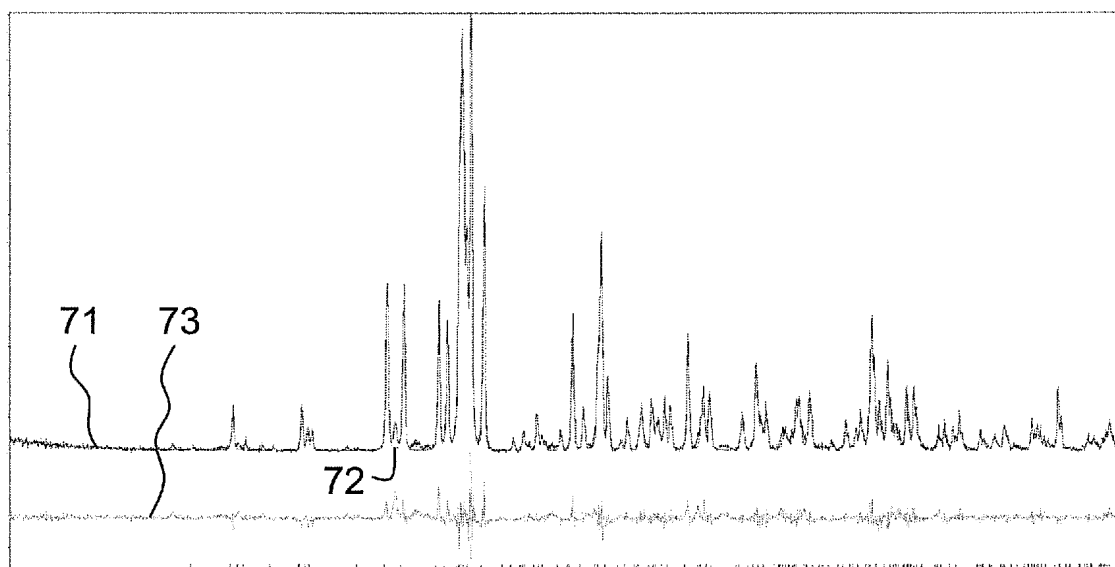
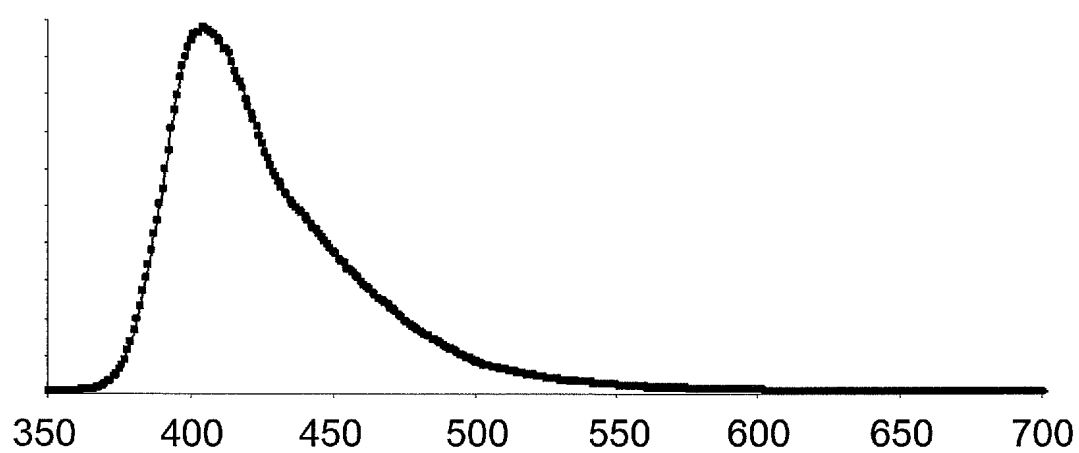
FIG. 2

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**FIG. 3****FIG. 4**

**FIG. 5****FIG. 6**

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**FIG. 7****FIG. 8**

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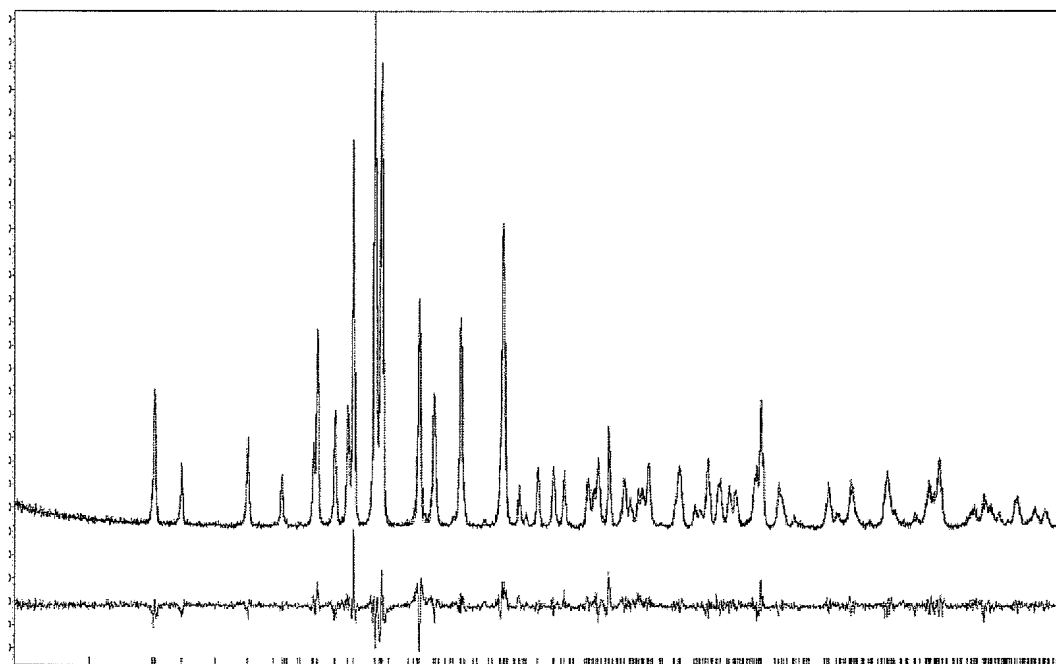


FIG. 9

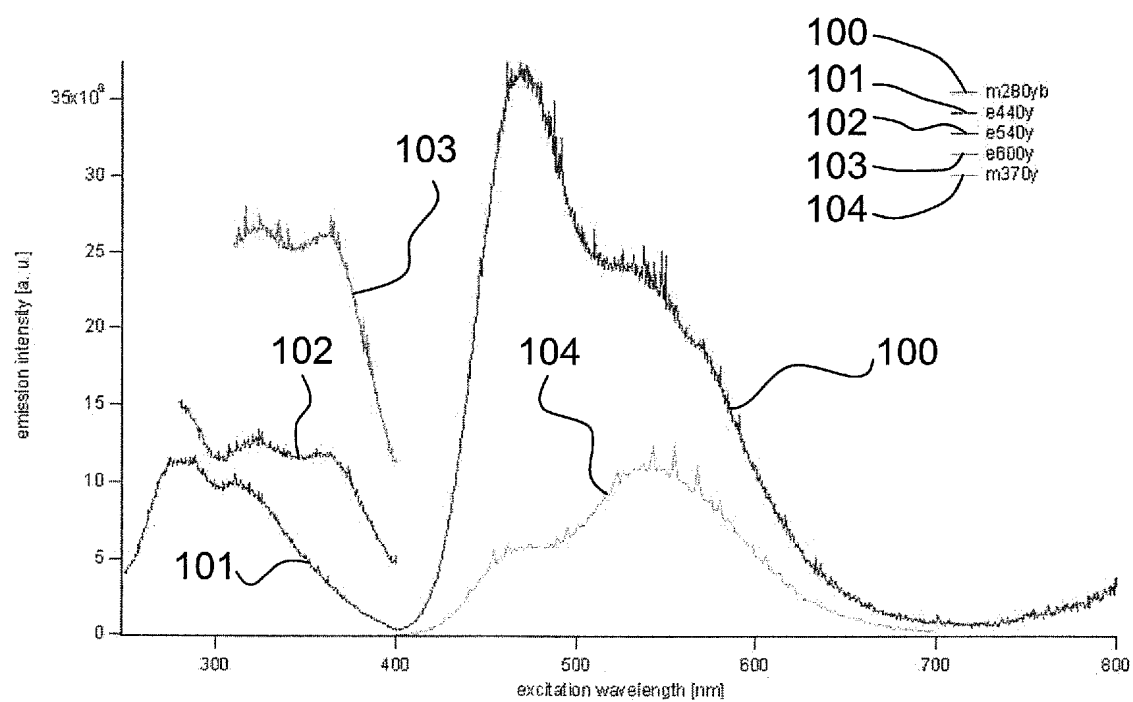


FIG. 10

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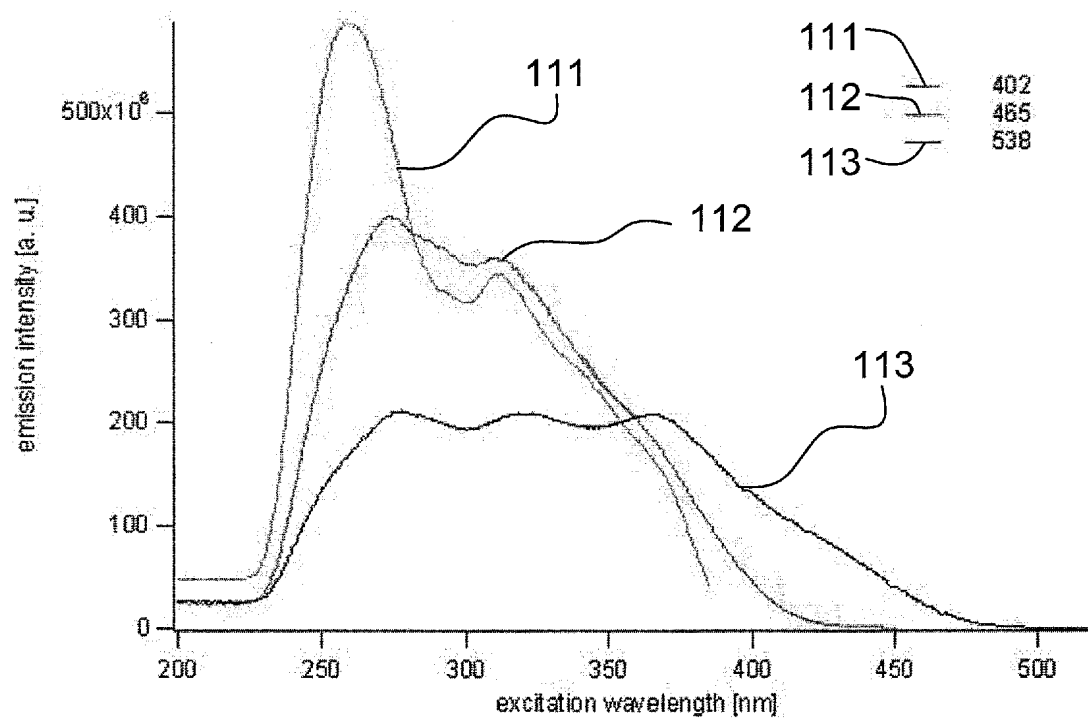


FIG. 11

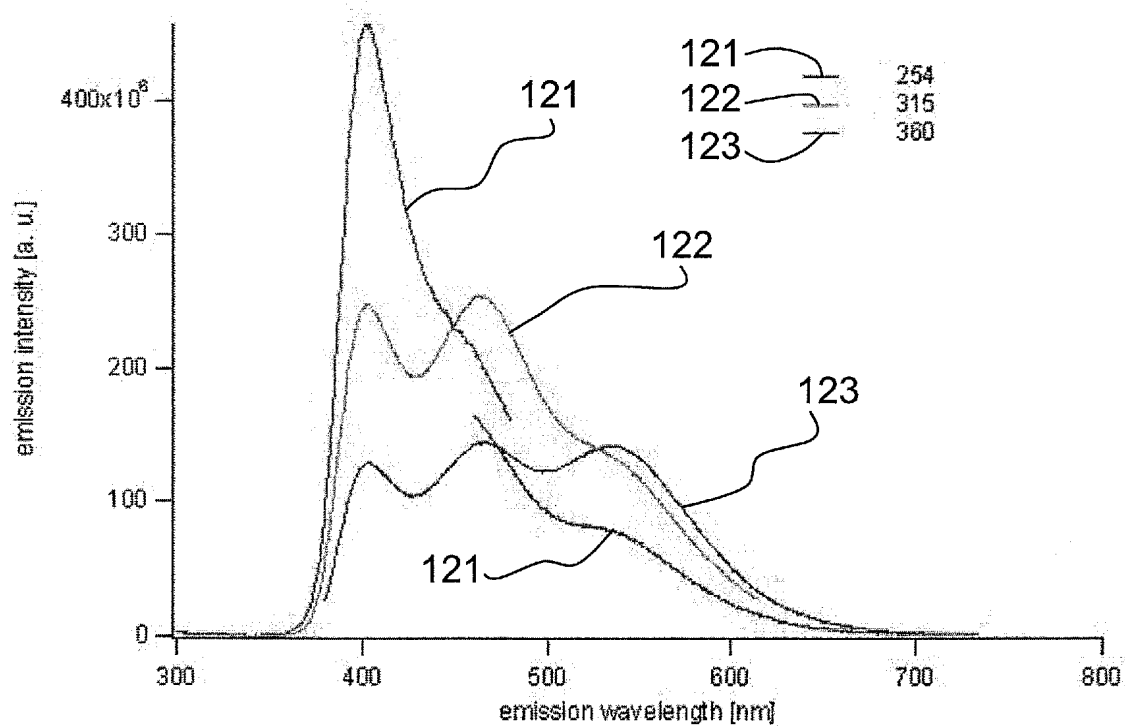


FIG. 12