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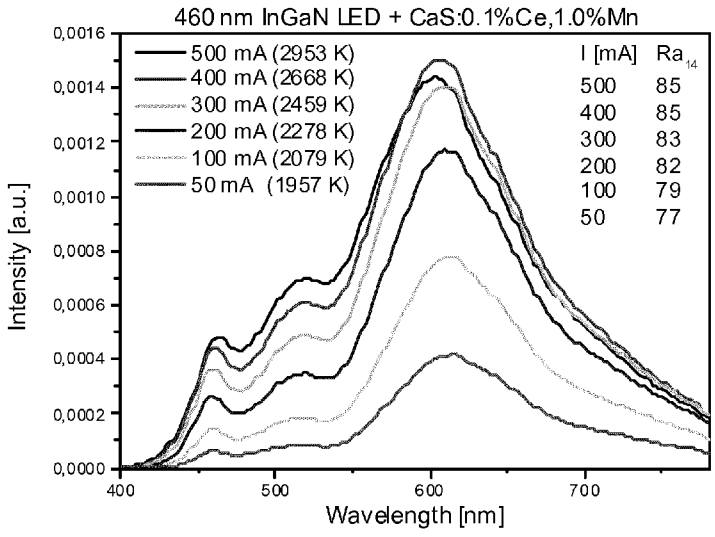
(54) Title: A WHITE LIGHT EMITTING SOLID STATE LIGHT SOURCE

Figure 2



(57) Abstract: Suggested is a white light emitting solid state light source exhibiting an incandescent-like dimming behaviour which is operated at an excitation density of about 0.1 to about 100 W/mm^2, comprising or consisting of (a) a primary light source; (b) a luminescent layer capable of emitting primary radiation deposited on said primary light source, and (c) a luminescent screen capable of converting said primary radiation into radiation suitable for the addressed illumination application, wherein said luminescent layer comprises at least one phosphor that is activated by at least two cations selected from the group consisting of Ce^{3+}, Mn^{2+}, Pr^{3+}, and Eu^{2+}.

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A White Light Emitting Solid State Light Source

Field of Invention

[0001] This present invention relates to specific solid state light sources with incandescent dimming behaviour, and more particularly to semiconductor light emitting diodes (LEDs), laser diodes (LDs), or organic light emitting diodes (OLEDs), comprising luminescent screens for the conversion of the primary radiation into radiation suitable for the addressed illumination application.

State of the Art

[0002] Presently, white light emitting solid state light sources mostly comprises a high brightness blue light emitting semiconductor chip based on (In,Ga)N [see S. Nakamura et al., Appl. Phys. Lett. 67, p 1868 (1995)] and a luminescent screen. The light source works as an efficient pump exciting a luminescent material which returns to its ground state by emitting green, yellow, or red light. Additive colour mixing results in a broadband emission spectrum which is perceived as white light. The principle of this colour conversion process is well-founded in the pronounced Stokes Shift (electron-phonon coupling) between absorption and emission of electromagnetic radiation.

[0003] Already in 1996, Nichia Chemical Industries Ltd. introduced a white LED, that uses a luminescent layer comprising $Y_3Al_5O_{12}$:Ce (YAG:Ce) or $Y_3(Al_{1-x}Ga_x)_5O_{12}$:Ce (YAGaG:Ce) to convert blue light emitted by an (In,Ga)N LED into a broad band yellow emission spectrum, that peaks at about 565 nm. The emission band is sufficiently broad to produce white light in the colour temperature range from about 5,000 to about 8,000 K, and a colour rendering index (CRI) of about 77 - 85.

[0004] The shortcoming of a luminescent layer comprising a single phosphor doped with a distinct activator is that colour rendering of the white LED depends on the adjusted colour temperature. In addition, very low colour temperatures with a sufficiently high colour rendering index cannot

be achieved by the application of YAG:Ce or YaGAG:Ce phosphors due to their lack of red emission. However, indoor lighting applications require white light sources with a much lower, incandescent lamp like colour temperature, and in addition to that a dimming behaviour similar to that of an incandescent lamp. In other words what required is a light source providing increasing colour temperature by increasing driving current. While the former requirement was already addressed by many LED manufacturers, e.g. by the introduction of $CaAlSiN_3$:Eu as a second phosphor, that emits between 600 and 700 nm, the latter process is hardly addressed so far.

[0005] Therefore, it has been the object of the present invention to provide a solid state light source that overcomes the disadvantages of the state of the art as described above. In particular, the spectral properties and dimming behaviour similar to those known from incandescent lamps.

Description of the Invention

[0006] A first object of the present invention is directed to is a white light emitting solid state light source exhibiting an incandescent-like dimming behaviour which is adapted to be operated at an excitation density of about 0.1 to about 100 W/mm^2, preferably about 0.5 to about 50 W/mm^2 and most preferred about 1 to about 20 W/mm^2 comprising or consisting of

(a) a primary light source;

(b) a luminescent layer capable of emitting primary radiation deposited on said primary light source, and

(c) a luminescent screen capable of converting said primary radiation into radiation suitable for the addressed illumination application,

wherein

said luminescent layer comprises at least one phosphor that is activated by at least two cations selected from the group consisting of Ce^{3+}, Mn^{2+}, Pr^{3+} and Eu^{2+}.

[0007] For the sake of good order it should be mentioned that in the course of the present invention excitation density is determined according

to DIN 50564/VDE 0705-2301 ("Messung niedriger Leistungsaufnahmen"/"Determination of low power uptakes")

[0008] Surprisingly, it has been observed that a solid light source according to the present invention comprising a phosphor in its luminescent layer that is co-activated by specific ion couples comprising Ce^{3+}, Mn^{2+}, Pr^{3+} and Eu^{2+} display luminescence in the green to red spectral range, whereby the long decay time of Mn^{2+} results in bleaching of the Mn^{2+} upon a high excitation density.

[0009] More particularly it has been observed that the claimed light source exhibits spectral properties and dimming behaviour similar to those known from incandescent lamps. In particular, the colour temperature is rather low, typically below 3,000 K, while dimming behaviour is equal to that of (halogen) incandescent lamps, due to the specific properties of the luminescent screen. In other words, the colour point shifts to lower temperatures along the black body line, if the lamp is dimmed. Such a solid state light source are required for those illumination areas in which an incandescent lamp like dimming behaviour is required, e.g. where cosy indoor illumination is desired.

[0010] Therefore, the present invention fulfils all requirements to solve the problem as described above.

[0011] Primary Light Sources

[0012] The primary light source of the present invention is either a semiconductor LED, a semiconductor laser diode (LD) or an organic light emitting diode (OLED). More particularly preferred are those sources emitting light within the spectral range of about 385 to about 480 nm, preferably about 390 to about 450 nm and most preferred about 400 to 440 nm.

[0013] Over all, the light sources according to the present invention are in particular characterized by

- being capable of emitting two emission bands,

- exhibiting increasing colour temperature by increasing driving current, and/or
- exhibiting a shift of its colour point towards higher colour temperatures by enhancing power density.

[0014] Light emitting diodes (LED)

[0015] A light-emitting diode (LED) forming a first group of suitable primary light sources, is a two-lead semiconductor light source. It is a p–n junction diode, which emits light when activated. When a suitable voltage is applied to the leads, electrons are able to recombine with electron holes within the device, releasing energy in the form of photons. This effect is called electroluminescence, and the colour of the light (corresponding to the energy of the photon) is determined by the energy band gap of the semiconductor.

[0016] A p-n junction can convert absorbed light energy into a proportional electric current. The same process is reversed here (i.e. the p-n junction emits light when electrical energy is applied to it). This phenomenon is generally called electroluminescence, which can be defined as the emission of light from a semi-conductor under the influence of an electric field. The charge carriers recombine in a forward-biased p-n junction as the electrons cross from the n-region and recombine with the holes existing in the p-region. Free electrons are in the conduction band of energy levels, while holes are in the valence energy band. Thus the energy level of the holes will be lesser than the energy levels of the electrons. Some portion of the energy must be dissipated in order to recombine the electrons and the holes. This energy is emitted in the form of heat and light.

[0017] The electrons dissipate energy in the form of heat for silicon and germanium diodes but in gallium arsenide phosphide (GaAsP) and gallium phosphide (GaP) semiconductors, the electrons dissipate energy by emitting photons. If the semiconductor is translucent, the junction becomes the source of light as it is emitted, thus becoming a light-emitting diode, but

when the junction is reverse biased no light will be produced by the LED and, on the contrary, the device may also be damaged.

[0018] Typically, The LED consists of a chip of semiconducting material doped with impurities to create a p-n junction. As in other diodes, current flows easily from the p-side, or anode, to the n-side, or cathode, but not in the reverse direction. Charge-carriers-electrons and holes-flow into the junction from electrodes with different voltages. When an electron meets a hole, it falls into a lower energy level and releases energy in the form of a photon.

[0019] The wavelength of the light emitted, and thus its colour, depends on the band gap energy of the materials forming the p-n junction.
In silicon or germanium diodes, the electrons and holes usually recombine by a non-radiative transition, which produces no optical emission, because these are indirect band gap materials. The materials used for the LED have a direct band gap with energies corresponding to near-infrared, visible, or near-ultraviolet light.

[0020] LEDs are usually built on an n-type substrate, with an electrode attached to the p-type layer deposited on its surface. P-type substrates, while less common, occur as well. Many commercial LEDs, especially GaN/InGaN, also use sapphire substrate.

[0021] Most materials used for LED production have very high refractive indices. This means that much of the light will be reflected back into the material at the material/air surface interface. Thus, light extraction in LEDs is an important aspect of LED production, subject to much research and development.

[0022] For example, bare uncoated semiconductors such as silicon exhibit a very high refractive index relative to open air, which prevents passage of photons arriving at sharp angles relative to the air-contacting surface of the semiconductor due to total internal reflection. This property affects both the light-emission efficiency of LEDs as well as the light-absorption efficiency of photovoltaic cells. The refractive index of silicon is 3.96 (at 590 nm), while air is 1.0002926.

[0023] In general, a flat-surface uncoated LED semiconductor chip will emit light only perpendicular to the semiconductor's surface, and a few degrees to the side, in a cone shape referred to as the *light cone*, *cone of light*, or the *escape cone*. The maximum angle of incidence is referred to as the critical angle. When this angle is exceeded, photons no longer escape the semiconductor but are instead reflected internally inside the semiconductor crystal as if it were a mirror.

[0024] Internal reflections can escape through other crystalline faces, if the incidence angle is low enough and the crystal is sufficiently transparent to not re-absorb the photon emission. But for a simple square LED with 90-degree angled surfaces on all sides, the faces all act as equal angle mirrors. In this case most of the light cannot escape and is lost as waste heat in the crystal.

[0025] A convoluted chip surface with angled facets similar to a jewel or Fresnel lens can increase light output by allowing light to be emitted perpendicular to the chip surface while far to the sides of the photon emission point. The ideal shape of a semiconductor with maximum light output would be a microsphere with the photon emission occurring at the exact centre, with electrodes penetrating to the centre to contact at the emission point. All light rays emanating from the centre would be perpendicular to the entire surface of the sphere, resulting in no internal reflections. A hemispherical semiconductor would also work, with the flat back-surface serving as a mirror to back-scattered photons.

[0026] A preferred embodiment of the present invention encompasses so-called “Chip-on-board” (COB) LED comprising one or more chips. Particularly useful are COB according to the following geometry: diameter of the ring: about 1 to about 10 and preferably about 5 mm around the ring. Once the ring is filled its height is about 0.5 mm resulting in a volume of ab 10 mm^3. In a typical embodiment said chips show a feed size of about 800 to about 1,200 µm and preferably of about 1,000 µm corresponding to an area of about 1 mm^2. The free space above the chip amounts to about 200 to about 300 µm and preferably about 250 µm, which is equivalent to the

magnitude of the phosphor layer above the surface of said chips. Depending on colour temperature the phosphors useful for operating COB chips comprise about 10 to about 100 mg and preferably about 20 mg silicones corresponding to an amount of up to 50 % of said phosphor or a mass of up to 10 mg, which are distributed over an area of about 10 mm^2 and a volume of about 20 mm^3.

[0027] Laser diodes (LD)

[0028] A laser diode, or LD also known as injection laser diode or ILD, is an electrically pumped semiconductor laser in which the active laser medium is formed by a p-n junction of a semiconductor diode similar to that found in a light-emitting diode.

[0029] The laser diode is the most common type of laser produced with a wide range of uses that include fibre optic communications, barcode readers, laser pointers, CD/DVD/Blu-ray Disc reading and recording, laser printing, laser scanning and increasingly directional lighting sources.

[0030] From an electronic point of view a laser diode is a PIN diode. The active region of the laser diode is in the intrinsic (I) region and the carriers (electrons and holes) are pumped into that region from the N and P regions respectively. While initial diode laser research was conducted on simple P-N diodes, all modern lasers use the double-heterostructure implementation, where the carriers and the photons are confined in order to maximize their chance for recombination and light generation. Unlike a regular diode, the goal for a laser diode is to recombine all carriers in the I region, and produce light. Thus, laser diodes are fabricated using direct bandgap semiconductors. The laser diode epitaxial structure is grown using one of the crystal growth techniques, usually starting from an N doped substrate, and growing the I doped active layer, followed by the P doped cladding, and a contact layer. The active layer most often consists of quantum wells, which provide lower threshold current and higher efficiency.

[0031] Laser diodes form a subset of the larger classification of semiconductor p-n junction diodes. Forward electrical bias across the laser

diode causes the two species of charge carrier – holes and electrons – to be "injected" from opposite sides of the *p-n* junction into the depletion region. Holes are injected from the *p*-doped, and electrons from the *n*-doped, semiconductor. (A depletion region, devoid of any charge carriers, forms as a result of the difference in electrical potential between *n*- and *p*-type semiconductors wherever they are in physical contact.) Due to the use of charge injection in powering most diode lasers, this class of lasers is sometimes termed "injection lasers," or "injection laser diode" (ILD). As diode lasers are semiconductor devices, they may also be classified as semiconductor lasers. Either designation distinguishes diode lasers from solid-state lasers.

[0032] Another method of powering some diode lasers is the use of optical pumping. Optically pumped semiconductor lasers (OPSL) use a III-V semiconductor chip as the gain medium, and another laser (often another diode laser) as the pump source. OPSL offer several advantages over ILDs, particularly in wavelength selection and lack of interference from internal electrode structures.

[0033] When an electron and a hole are present in the same region, they may recombine or "annihilate" producing a spontaneous emission — i.e., the electron may re-occupy the energy state of the hole, emitting a photon with energy equal to the difference between the electron's original state and hole's state. (In a conventional semiconductor junction diode, the energy released from the recombination of electrons and holes is carried away as phonons, i.e., lattice vibrations, rather than as photons.) Spontaneous emission below the lasing threshold produces similar properties to an LED. Spontaneous emission is necessary to initiate laser oscillation, but it is one among several sources of inefficiency once the laser is oscillating.

[0034] The difference between the photon-emitting semiconductor laser and a conventional phonon-emitting (non-light-emitting) semiconductor junction diode lies in the type of semiconductor used, one whose physical and atomic structure confers the possibility for photon emission. These photon-emitting semiconductors are the so-called "direct bandgap"

semiconductors. The properties of silicon and germanium, which are single-element semiconductors, have bandgaps that do not align in the way needed to allow photon emission and are not considered "direct." Other materials, the so-called compound semiconductors, have virtually identical crystalline structures as silicon or germanium but use alternating arrangements of two different atomic species in a checkerboard-like pattern to break the symmetry. The transition between the materials in the alternating pattern creates the critical "direct bandgap" property. Gallium arsenide, indium phosphide, gallium antimonide, and gallium nitride are all examples of compound semiconductor materials that can be used to create junction diodes that emit light.

[0035] In the absence of stimulated emission (e.g., lasing) conditions, electrons and holes may coexist in proximity to one another, without recombining, for a certain time, termed the "upper-state lifetime" or "recombination time" (about a nanosecond for typical diode laser materials), before they recombine. A nearby photon with energy equal to the recombination energy can cause recombination by stimulated emission. This generates another photon of the same frequency, polarization, and phase , travelling in the same direction as the first photon. This means that stimulated emission will cause gain in an optical wave (of the correct wavelength) in the injection region, and the gain increases as the number of electrons and holes injected across the junction increases. The spontaneous and stimulated emission processes are vastly more efficient in direct bandgap semiconductors than in indirect bandgap semiconductors; therefore silicon is not a common material for laser diodes.

[0036] As in other lasers, the gain region is surrounded with an optical cavity to form a laser. In the simplest form of laser diode, an optical waveguide is made on that crystal's surface, such that the light is confined to a relatively narrow line. The two ends of the crystal are cleaved to form perfectly smooth, parallel edges, forming a Fabry–Pérot resonator. Photons emitted into a mode of the waveguide will travel along the waveguide and be reflected several times from each end face before they exit. As a light

wave passes through the cavity, it is amplified by stimulated emission, but light is also lost due to absorption and by incomplete reflection from the end facets. Finally, if there is more amplification than loss, the diode begins to "lase".

[0037] Some important properties of laser diodes are determined by the geometry of the optical cavity. Generally, the light is contained within a very thin layer, and the structure supports only a single optical mode in the direction perpendicular to the layers. In the transverse direction, if the waveguide is wide compared to the wavelength of light, then the waveguide can support multiple transverse optical modes, and the laser is known as "multi-mode". These transversely multi-mode lasers are adequate in cases where one needs a very large amount of power, but not a small diffraction-limited beam; for example in printing, activating chemicals, or pumping other types of lasers.

[0038] In applications where a small focused beam is needed, the waveguide must be made narrow, on the order of the optical wavelength. This way, only a single transverse mode is supported and one ends up with a diffraction-limited beam. Such single spatial mode devices are used for optical storage, laser pointers, and fiber optics. Note that these lasers may still support multiple longitudinal modes, and thus can lase at multiple wavelengths simultaneously. The wavelength emitted is a function of the band-gap of the semiconductor material and the modes of the optical cavity. In general, the maximum gain will occur for photons with energy slightly above the band-gap energy, and the modes nearest the peak of the gain curve will lase most strongly. The width of the gain curve will determine the number of additional "side modes" that may also lase, depending on the operating conditions. Single spatial mode lasers that can support multiple longitudinal modes are called Fabry Perot (FP) lasers. An FP laser will work at multiple cavity modes within the gain bandwidth of the lasing medium. The number of lasing modes in an FP laser is usually unstable, and can fluctuate due to changes in current or temperature.

[0039] Single spatial mode diode lasers can be designed so as to operate on a single longitudinal mode. These single frequency diode lasers exhibit a high degree of stability, and are used in spectroscopy and metrology, and as frequency references. Single frequency diode lasers classed as either distributed feedback (DFB) lasers or distributed Bragg reflector (DBR) lasers.

[0040] The explanations provided above are intended to illustrate the working principle of a LD. However, devices operating accordingly would be very inefficient, since they require so much power that they can only achieve pulsed operation without damage. Therefore, the simple diode described above has been heavily modified in recent years to accommodate modern technology, resulting in a variety of types of laser diodes, as described below:

[0041] **Double heterostructure laser (DH Laser).** In these devices, a layer of low bandgap material is sandwiched between two high bandgap layers. One commonly-used pair of materials is gallium arsenide (GaAs) with aluminium gallium arsenide ($Al_xGa_{(1-x)}As$). Each of the junctions between different bandgap materials is called a *heterostructure*, hence the name "double heterostructure laser" or *DH* laser. The kind of laser diode described in the first part of the article may be referred to as a *homojunction* laser, for contrast with these more popular devices. The advantage of a DH laser is that the region where free electrons and holes exist simultaneously—the active region—is confined to the thin middle layer. This means that many more of the electron-hole pairs can contribute to amplification—not so many are left out in the poorly amplifying periphery. In addition, light is reflected from the heterojunction; hence, the light is confined to the region where the amplification takes place.

[0042] **Quantum Well Lasers (QWL).** If the middle layer is made thin enough, it acts as a quantum well. This means that the vertical variation of the electron's wave-function, and thus a component of its energy, is quantized. The efficiency of a quantum well laser is greater than that of a bulk laser because the density of states function of electrons in the

quantum well system has an abrupt edge that concentrates electrons in energy states that contribute to laser action. Lasers containing more than one quantum well layer are known as *multiple quantum well* lasers. Multiple quantum wells improve the overlap of the gain region with the optical waveguide mode. Further improvements in the laser efficiency have also been demonstrated by reducing the quantum well layer to a quantum wire or to a "sea" of quantum dots.

[0043] Quantum Cascade Lasers (QCL). In a quantum cascade laser, the difference between quantum well energy levels is used for the laser transition instead of the bandgap. This enables laser action at relatively long wavelengths, which can be tuned simply by altering the thickness of the layer. They are heterojunction lasers.

[0044] Interband Cascade Lasers (ICL). An interband cascade laser (ICL) is a type of laser diode that can produce coherent radiation over a large part of the mid-infrared region of the electromagnetic spectrum. The problem with the simple quantum well diode described above is that the thin layer is simply too small to effectively confine the light. To compensate, another two layers are added on, outside the first three. These layers have a lower refractive index than the centre layers, and hence confine the light effectively. Such a design is called a separate confinement heterostructure (SCH) laser diode. Almost all commercial laser diodes since the 1990s have been SCH quantum well diodes.

[0045] Distributed Bragg Reflector Laser (DBR). A distributed Bragg reflector laser (DBR) is a type of single frequency laser diode. It is characterized by an optical cavity consisting of an electrically or optically pumped gain region between two mirrors to provide feedback. One of the mirrors is a broadband reflector and the other mirror is wavelength selective so that gain is favoured on a single longitudinal mode, resulting in lasing at a single resonant frequency. The broadband mirror is usually coated with a low reflectivity coating to allow emission. The wavelength selective mirror is a periodically structured diffraction grating with high reflectivity. The diffraction grating is within a non-pumped, or passive region of the cavity. A

DBR laser is a monolithic single chip device with the grating etched into the semiconductor. DBR lasers can be edge emitting lasers or VCSELs. Alternative hybrid architectures that share the same topology include extended cavity diode lasers and volume Bragg grating lasers, but these are not properly called DBR lasers.

[0046] Distributed Feedback Laser (DFL). A distributed feedback laser (DFB) is a type of single frequency laser diode. DFBs are the most common transmitter type in DWDM-systems. To stabilize the lasing wavelength, a diffraction grating is etched close to the p-n junction of the diode. This grating acts like an optical filter, causing a single wavelength to be fed back to the gain region and lase. Since the grating provides the feedback that is required for lasing, reflection from the facets is not required. Thus, at least one facet of a DFB is anti-reflection coated. The DFB laser has a stable wavelength that is set during manufacturing by the pitch of the grating, and can only be tuned slightly with temperature. DFB lasers are widely used in optical communication applications where a precise and stable wavelength is critical. The threshold current of this DFB laser, based on its static characteristic, is around 11 mA. The appropriate bias current in a linear regime could be taken in the middle of the static characteristic (50 mA).

[0047] VCSEL. Vertical-cavity surface-emitting lasers (VCSELs) have the optical cavity axis along the direction of current flow rather than perpendicular to the current flow as in conventional laser diodes. The active region length is very short compared with the lateral dimensions so that the radiation emerges from the surface of the cavity rather than from its edge. The reflectors at the ends of the cavity are dielectric mirrors made from alternating high and low refractive index quarter-wave thick multilayer. Such dielectric mirrors provide a high degree of wavelength-selective reflectance at the required free surface wavelength λ if the thicknesses of alternating layers d_1 and d_2 with refractive indices n_1 and n_2 are such that $n_1d_1 + n_2d_2 = \lambda/2$ which then leads to the constructive interference of all partially reflected waves at the interfaces. But there is a disadvantage: because of the high

mirror reflectivity, VCSELs have lower output powers when compared to edge-emitting lasers. There are several advantages to producing VCSELs when compared with the production process of edge-emitting lasers. Edge-emitters cannot be tested until the end of the production process. If the edge-emitter does not work, whether due to bad contacts or poor material growth quality, the production time and the processing materials have been wasted. Additionally, because VCSELs emit the beam perpendicular to the active region of the laser as opposed to parallel as with an edge emitter, tens of thousands of VCSELs can be processed simultaneously on a three-inch gallium arsenide wafer. Furthermore, even though the VCSEL production process is more labour- and material-intensive, the yield can be controlled to a more predictable outcome. However, they normally show a lower power output level.

[0048] VECSEL. Vertical external-cavity surface-emitting lasers, or VECSELs, are similar to VCSELs. In VCSELs, the mirrors are typically grown epitaxially as part of the diode structure, or grown separately and bonded directly to the semiconductor containing the active region. VECSELs are distinguished by a construction in which one of the two mirrors is external to the diode structure. As a result, the cavity includes a free-space region. A typical distance from the diode to the external mirror would be 1 cm. One of the most interesting features of any VECSEL is the small thickness of the semiconductor gain region in the direction of propagation, less than 100 nm. In contrast, a conventional in-plane semiconductor laser entails light propagation over distances of from 250 μm upward to 2 mm or longer. The significance of the short propagation distance is that it causes the effect of "anti-guiding" nonlinearities in the diode laser gain region to be minimized. The result is a large-cross-section single-mode optical beam which is not attainable from in-plane ("edge-emitting") diode lasers. Several workers demonstrated optically pumped VECSELs, and they continue to be developed for many applications including high power sources for use in industrial machining (cutting, punching, etc.) because of their unusually high power and efficiency when

pumped by multi-mode diode laser bars. However, because of their lack of p-n junction, optically-pumped VECSELs are not considered "diode lasers", and are classified as semiconductor lasers. Electrically pumped VECSELs have also been demonstrated. Applications for electrically pumped VECSELs include projection displays, served by frequency doubling of near-IR VECSEL emitters to produce blue and green light.

[0049] External Cavity Diode Lasers (EDL). Finally, external-cavity diode lasers are tunable lasers which use mainly double heterostructure diodes of the $Al_xGa_{(1-x)}As$ type. The first external-cavity diode lasers used intracavity etalons and simple tuning Littrow gratings. Other designs include gratings in grazing-incidence configuration and multiple-prism grating configurations.

[0050] Organic Light Emitting Diodes (OLED)

[0051] A third group of suitable primary light sources encompasses so-called organic light emitting diodes (OLED) in which the emissive electro-luminescent layer is a film of organic compound that emits light in response to an electric current. This layer of organic semiconductor is situated between two electrodes; typically, at least one of these electrodes is transparent. OLEDs are used to create digital displays in devices such as television screens, computer monitors, portable systems such as mobile phones, handheld game console sand PDAs. A major area of research is the development of white OLED devices for use in solid-state lighting applications.

[0052] There are two main families of OLED: those based on small molecules and those employing polymers. Adding mobile ions to an OLED creates a light-emitting electrochemical cell (LEC) which has a slightly different mode of operation. OLED displays can use either passive-matrix (PMOLED) or active-matrix (AMOLED) addressing schemes. Active-matrix OLEDs (AMOLED) require a thin-film transistor backplane to switch each individual pixel on or off, but allow for higher resolution and larger display sizes.

[0053] An OLED display works without a backlight; thus, it can display deep black levels and can be thinner and lighter than a liquid crystal display (LCD). In low ambient light conditions (such as a dark room), an OLED screen can achieve a higher contrast ratio than an LCD, regardless of whether the LCD uses cold cathode fluorescent lamps or an LED backlight.

[0054] A typical OLED is composed of a layer of organic materials situated between two electrodes, the anode and cathode, all deposited on a substrate. The organic molecules are electrically conductive as a result of delocalization of pi electrons caused by conjugation over part or all of the molecules. These materials have conductivity levels ranging from insulators to conductors, and are therefore considered organic semiconductors. The highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of organic semiconductors are analogous to the valence and conduction bands of inorganic semiconductors.

[0055] Originally, the most basic polymer OLEDs consisted of a single organic layer. However, multilayer OLEDs can be fabricated with two or more layers in order to improve device efficiency. As well as conductive properties, different materials may be chosen to aid charge injection at electrodes by providing a more gradual electronic profile or block a charge from reaching the opposite electrode and being wasted. Many modern OLEDs incorporate a simple bilayer structure, consisting of a conductive layer and an emissive layer. More recent developments in OLED architecture improve quantum efficiency (up to 19%) by using a graded heterojunction. In the graded heterojunction architecture, the composition of hole and electron-transport materials varies continuously within the emissive layer with a dopant emitter. The graded heterojunction architecture combines the benefits of both conventional architectures by improving charge injection while simultaneously balancing charge transport within the emissive region.

[0056] During operation, a voltage is applied across the OLED such that the anode is positive with respect to the cathode. Anodes are picked based

upon the quality of their optical transparency, electrical conductivity, and chemical stability. A current of electrons flows through the device from cathode to anode, as electrons are injected into the LUMO of the organic layer at the cathode and withdrawn from the HOMO at the anode. This latter process may also be described as the injection of electron holes into the HOMO. Electrostatic forces bring the electrons and the holes towards each other and they recombine forming an exciton, a bound state of the electron and hole. This happens closer to the emissive layer, because in organic semiconductors holes are generally more mobile than electrons. The decay of this excited state results in a relaxation of the energy levels of the electron, accompanied by emission of radiation whose frequency is in the visible region. The frequency of this radiation depends on the band gap of the material, in this case the difference in energy between the HOMO and LUMO.

[0057] As electrons and holes are fermions with half integer spin, an exciton may either be in a singlet state or a triplet state depending on how the spins of the electron and hole have been combined. Statistically three triplet excitons will be formed for each singlet exciton. Decay from triplet states (phosphorescence) is spin forbidden, increasing the timescale of the transition and limiting the internal efficiency of fluorescent devices. Phosphorescent organic light-emitting diodes make use of spin–orbit interactions to facilitate intersystem crossing between singlet and triplet states, thus obtaining emission from both singlet and triplet states and improving the internal efficiency.

[0058] Indium tin oxide (ITO) is commonly used as the anode material. It is transparent to visible light and has a high work function which promotes injection of holes into the HOMO level of the organic layer. A typical conductive layer may consist of PEDOT:PSS as the HOMO level of this material generally lies between the work function of ITO and the HOMO of other commonly used polymers, reducing the energy barriers for hole injection. Metals such as barium and calcium are often used for the cathode as they have low work functions which promote injection of electrons into

the LUMO of the organic layer. Such metals are reactive, so they require a capping layer of aluminium to avoid degradation.

[0059] Experimental research has proven that the properties of the anode, specifically the anode/hole transport layer (HTL) interface topography plays a major role in the efficiency, performance, and lifetime of organic light emitting diodes. Imperfections in the surface of the anode decrease anode-organic film interface adhesion, increase electrical resistance, and allow for more frequent formation of non-emissive dark spots in the OLED material adversely affecting lifetime. Mechanisms to decrease anode roughness for ITO/glass substrates include the use of thin films and self-assembled monolayers. Also, alternative substrates and anode materials are being considered to increase OLED performance and lifetime. Possible examples include single crystal sapphire substrates treated with gold (Au) film anodes yielding lower work functions, operating voltages, electrical resistance values, and increasing lifetime of OLEDs.

[0060] Single carrier devices are typically used to study the kinetics and charge transport mechanisms of an organic material and can be useful when trying to study energy transfer processes. As current through the device is composed of only one type of charge carrier, either electrons or holes, recombination does not occur and no light is emitted. For example, electron only devices can be obtained by replacing ITO with a lower work function metal which increases the energy barrier of hole injection. Similarly, hole only devices can be made by using a cathode made solely of aluminium, resulting in an energy barrier too large for efficient electron injection.

[0061] Efficient OLEDs using small molecules were first developed by C.W. Tang *et al.* at Eastman Kodak. The term OLED traditionally refers specifically to this type of *device*, though the term SM-OLED is also in use.

[0062] Molecules commonly used in OLEDs include organometallic chelates (for example Alq_3, used in the organic light-emitting device reported by Tang *et al.*), fluorescent and phosphorescent dyes and conjugated dendrimers. A number of materials are used for their charge

transport properties, for example triphenylamine and derivatives are commonly used as materials for hole transport layers. Fluorescent dyes can be chosen to obtain light emission at different wavelengths, and compounds such as perylene, rubrene and quinacridone derivatives are often used. Alq_3 has been used as a green emitter, electron transport material and as a host for yellow and red emitting dyes.

[0063] The production of small molecule devices and displays usually involves thermal evaporation in a vacuum. This makes the production process more expensive and of limited use for large-area devices, than other processing techniques. However, contrary to polymer-based devices, the vacuum deposition process enables the formation of well controlled, homogeneous films, and the construction of very complex multi-layer structures. This high flexibility in layer design, enabling distinct charge transport and charge blocking layers to be formed, is the main reason for the high efficiencies of the small molecule OLEDs.

[0064] Coherent emission from a laser dye-doped tandem SM-OLED device, excited in the pulsed regime, has been demonstrated. The emission is nearly diffraction limited with a spectral width similar to that of broadband dye lasers.

[0065] Polymer light-emitting diodes (PLED), also light-emitting polymers (LEP), involve an electroluminescent conductive polymer that emits light when connected to an external voltage. They are used as a thin film for full-spectrum colour displays. Polymer OLEDs are quite efficient and require a relatively small amount of power for the amount of light produced.

[0066] Vacuum deposition is not a suitable method for forming thin films of polymers. However, polymers can be processed in solution, and spin coating is a common method of depositing thin polymer films. This method is more suited to forming large-area films than thermal evaporation. No vacuum is required, and the emissive materials can also be applied on the substrate by a technique derived from commercial inkjet printing. However, as the application of subsequent layers tends to dissolve those already present, formation of multilayer structures is difficult with these

methods. The metal cathode may still need to be deposited by thermal evaporation in vacuum. An alternative method to vacuum deposition is to deposit a Langmuir-Blodgett film.

[0067] Typical polymers used in pleaded displays include derivatives of poly(*p*-phenylene vinylene) and polyfluorene. Substitution of side chains onto the polymer backbone may determine the colour of emitted light or the stability and solubility of the polymer for performance and ease of processing.

[0068] While unsubstituted poly(p-phenylene vinylene) (PPV) is typically insoluble, a number of PPVs and related poly(naphthalene vinylene)s (PNVs) that are soluble in organic solvents or water have been prepared via ring opening metathesis polymerization. These water-soluble polymers or conjugated poly electrolytes (CPEs) also can be used as hole injection layers alone or in combination with nanoparticles like graphene.

[0069] Phosphorescent organic light emitting diodes use the principle of electrophosphorescence to convert electrical energy in an OLED into light in a highly efficient manner, with the internal quantum efficiencies of such devices approaching 100%.

[0070] Typically, a polymer such as poly(N-vinylcarbazole) is used as a host material to which an organometallic complex is added as a dopant. Iridium complexes such as $Ir(mppy)_3$ are currently the focus of research, although complexes based on other heavy metals such as platinum have also been used.

[0071] The heavy metal atom at the centre of these complexes exhibits strong spin-orbit coupling, facilitating intersystem crossing between singlet and triplet states. By using these phosphorescent materials, both singlet and triplet excitons will be able to decay radiatively, hence improving the internal quantum efficiency of the device compared to a standard pleaded where only the singlet states will contribute to emission of light.

[0072] Applications of OLEDs in solid state lighting require the achievement of high brightness with good CIE coordinates (for white emission). The use of macromolecular species like polyhedral oligomeric

silsesquioxanes (POSS) in conjunction with phosphorescent species such as Ir^{3+} for printed OLEDs has exhibited brightness as high as 10,000 cd/m^2.

[0073] The organic electroluminescent device according to the invention particularly preferably has the following structure: anode / orange- or red-phosphorescent emitter layer / interlayer 1 / interlayer 2 / cathode. Examples of suitable emitters are revealed by the applications WO 00/70655, WO 01/41512, WO 02/02714, WO 02/15645, EP 1191613, EP 1191612, EP 1191614, WO 04/081017, WO 05/033244, WO 05/042550, WO 05/113563, WO 06/008069, WO 06/061182, WO 06/081973. In general, all phosphorescent complexes as used in accordance with the prior art for phosphorescent OLEDs and as are known to the person skilled in the art in the area of organic electroluminescence are suitable, and the person skilled in the art will be able to use further phosphorescent compounds without inventive step. In particular, the person skilled in the art knows which phosphorescent complexes emit with what emission colour.

[0074] Suitable matrix materials for the phosphorescent compound are various materials as used in accordance with the prior art as matrix materials for phosphorescent compounds. Suitable matrix materials for the phosphorescent emitter are aromatic ketones, in particular selected from compounds of the formula (1) depicted above or aromatic phosphine oxides or aromatic sulfoxides or sulfones, for example in accordance with WO 04/013080, WO 04/093207 or WO 06/005627, triarylamines, carbazole derivatives, for example CBP (N,N-biscarbazolylbiphenyl), mCBP or the carbazole derivatives disclosed in WO 05/039246, US 2005/0069729, JP 2004/288381, EP 1205527 or WO 08/086851, indolocarbazole derivatives, for example in accordance with WO 07/063754 or WO 08/056746, azacarbazole derivatives, for example in accordance with EP 1617710, EP 1617711, EP 1731584, JP 2005/347160, bipolar matrix materials, for example in accordance with WO 07/137725, silanes, for example in accordance with WO 05/111172, azaboroles or boronic esters, for example in accordance with WO 06/117052, triazine derivatives, for

example in accordance with the unpublished application DE 102008036982.9, WO 07/063754 or WO 08/056746, zinc complexes, for example in accordance with EP 652273 or WO 09/062578, or diazasilole or tetraazasilole derivatives, for example in accordance with DE 102008056688 A.

[0075] Semiconductors

[0076] Semiconductors forming an essential part of the light sources of the present invention are selected from the group of species capable of emitting radiation in the blue spectral range, such as for example ZnSe, or SiC. The preferred semiconductors, however, are chosen either from GaN or (In,Ga)N. The most preferred OLED are based on Ir^{3+}, Pt^{2+}, or Cu^{+} emitters.

[0077] Luminescent Layer, Ion Couple Activators and Phosphors

[0078] Preferably the luminescent layer according to the present invention is capable of emitting primary radiation in the green to red spectral range (about 500 to about 700 nm). However, as explained above, the key to the invention is that said luminescent layer comprises at least one phosphor containing two different activator ions for the application as a colour conversion screen onto blue light emitting radiation sources, e.g. based onto an InGaN LED, an InGaN laser diode, or onto an organic light emitting diode (OLED).

[0079] The phosphors used in the luminescent layer give rise to good LED qualities. The LED quality is described here via conventional parameters, such as the colour rendering index (CRI), the correlated colour temperature (CCT), lumen equivalent, absolute lumen flux, or the colour point in CIE1931 x and y coordinates.

[0080] The colour rendering index (CRI) is a dimensionless lighting quantity, familiar to the person skilled in the art, which compares the colour reproduction faithfulness of an artificial light source with that of solar light or filament light sources (the latter two have a CRI of 100).

[0081] The correlated colour temperature (CCT) is a lighting quantity, familiar to the person skilled in the art, with the unit Kelvin. The higher the numerical value, the higher the blue content of the light and the colder the white light from an artificial radiation source appears to the observer. The CCT follows the concept of the black body radiator, whose colour temperature describes the so-called Planck curve in the CIE diagram.

[0082] The lumen equivalent is a lighting quantity, familiar to the person skilled in the art, with the unit lm/W which describes the magnitude of the photometric luminous flux in lumens of a light source at a certain radiometric radiation power with the unit watt. The higher the lumen equivalent, the more efficient a light source.

[0083] The lumen is a photometric lighting quantity, familiar to the person skilled in the art, which describes the luminous flux of a light source, which is a measure of the total visible radiation emitted by a radiation source. The greater the luminous flux, the brighter the light source appears to the observer.

[0084] CIE x and CIE y stand for the coordinates in the standard CIE colour chart (here standard observer 1931), familiar to the person skilled in the art, by means of which the colour of a light source is described.

[0085] All the quantities mentioned above can be calculated from the emission spectra of the light source by methods familiar to the person skilled in the art.

[0086] In the context of this application, UV light denotes light whose emission maximum is ≤ 400 nm, near UV light denotes light whose emission maximum is between 370-400nm, violet light denotes light whose emission maximum is between 401 and 430 nm, blue light denotes light whose emission maximum is between 431 and 470 nm, cyan-coloured light denotes light whose emission maximum is between 471 and 505 nm, green light denotes light whose emission maximum is between 506 and 560 nm, yellow light denotes light whose emission maximum is between 561 and 575 nm, orange light denotes light whose emission maximum is between

576 and 600 nm and red light denotes light whose emission maximum is between 601 and 700 nm.

[0087] Ion couple activators

[0088] Particularly, the following ion pair couples are found rather useful in a luminescent composition:

- Eu^{2+}/Mn^{2+}
- Ce^{3+}/Mn^{2+}
- Pr^{3+}/Mn^{2+}

[0089] Luminescent compositions doped by one of these ion couples, solely absorb blue light due to the sensitizing ions, i.e. Eu^{2+} and Ce^{3+}, respectively, since Mn^{2+} does not exhibit states in the blue spectral range with sufficient absorption cross section. The luminescent compositions can be excited over a broad range, which extends from about 300 nm to 440 nm, preferably 350 nm to about 420 nm. The maximum of the excitation curve is usually at about 350 to 400 nm, depending on the exact composition.

[0090] After the excitation process, green or yellow luminescence of Eu^{2+} or Ce^{3+} is observed. In addition, part of the absorbed energy is transferred to Mn^{2+} (energy transfer). In this way, a luminescent composition exhibiting two emission bands is obtained (see **Fig. 1**). The ratio of the two emission bands is dependent on the Mn^{2+} concentration (see **Fig. 4**) and on the excitation density. The latter dependence is caused by the rather short decay time of Eu^{2+} (about 1 µs) and Ce^{3+} (about 50 ns) and the long decay time of Mn^{2+}, which is in the millisecond range (5 to 50 ms), due to the spin-forbidden character of the respective electronic [Ar]3d5 towards [Ar]3d5 transitions.

[0091] The ion couple concept for the production of white light was already exploited by the invention of the phosphor $Ca_5(PO_4)_3(F,Cl)$:Sb,Mn, also called halophosphate. It is widely applied in linear fluorescent lamps. However, the energy transfer rate from Sb^{3+} to Mn^{2+} in these halophosphates is not dependent on the fluorescent lamp driving

conditions, since the excitation density is in all kind of lamps not higher than 0.1 W/mm^2 and thus much too low for the saturation of the Mn^{2+} emission, which would result in a blue shift of the colour point. The luminescent layer, which is deposited onto a blue-emitting semiconductor LED, is exposed to a very high excitation density, viz. 0.1 – 100 W/mm^2, and thus saturation of the Mn^{2+} emission will be observed. Therefore, a blue shift of the colour point by enhancing the driving current can be expected. This will be even more pronounced, if laser diodes will be used as a pump source.

[0092] In a specific embodiment the present invention is exemplified by a white light emitting pcLED employing CaS:Ce,Mn as a colour converter. The colour point of such a pcLED shifts to the blue by enhancing the driving current and to the red by reducing the driving current (**Fig. 2** and **Fig. 3**). According to this, the dimming behaviour of this pcLED is similar to what is observed for incandescent and halogen lamps and natural daylight at dusk and dawn. As indicated above, this feature is desired in all application areas, where incandescent or halogen lamps are replaced due to energy saving reasons. Presently, mostly integrated compact fluorescent lamps (CFLi), also called energy saving lamps, are installed for this purpose, although the colour point of this lamp type shifts to the blue if the driving current is reduced.

[0093] Phosphors

[0094] The selection of suitable phosphors is little critical, preferred are those, however, capable of emitting radiation in the orange or red part of the spectrum.

[0095] In a first embodiment suitable phosphors are selected from the group consisting of oxides, nitrides, oxynitrides, sulphides, oxysulfides and their mixtures. Particularly preferred are silicates, alumosilicates and garnets preferably selected from the group consisting of $(Y,Gd,Tb,Lu)_3Al_{5-x}Si_xO_{12-x}N_x$:X,Y ($0 \leq x \leq 5$), $BaMgAl_{10}O_{17}$:X,Y, $SrAl_2O_4$:X,Y, $Sr_4Al_{14}O_{25}$:X,Y, $(Ca,Sr,Ba)Si_2N_2O_2$:Eu, $SrSiAl_2O_3N_2$:X,Y, $(Ca,Sr,Ba)_2Si_5N_8$:X,Y, $(Ca,Sr,Ba)SiN_2$:X,Y, $CaAlSiN_3$:X,Y, $(Ca,Sr,Ba)_2SiO_4$:X,Y and other silicates,

molybdates, tungstates, vanadates, group III nitrides, oxides, in each case individually or mixtures thereof with at least two activator ions X and Y selected from Ce^{3+}, Mn^{2+}, Pr^{3+} and Eu^{2+}, as disclosed for example in US 8,946,982.

[0096] In still a further embodiment, the phosphors may be coated. Suitable for this purpose are all coating methods as are known to the person skilled from the prior art and are used for phosphors. Suitable materials for the coating are, in particular, metal oxides and nitrides, in particular alkaline-earth metal oxides, such as Al_2O_3, and alkaline-earth metal nitrides, such as AlN, as well as SiO_2. The coating can be carried out here, for example, by fluidised-bed methods or by wet-chemical methods. Suitable coating methods are disclosed, for example, in JP 04-304290, WO 91/10715, WO 99/27033, US 2007/0298250, WO 2009/065480 and WO 2010/075908. The aim of the coating can on the one hand be higher stability of the phosphors, for example to air or moisture. However, the aim may also be improved coupling-in and -out of light through a suitable choice of the surface of the coating and the refractive indices of the coating material. As an alternative or in addition to an inorganic coating, the phosphors may also be coated with organic materials, for example with siloxanes. This may have advantages with respect to the dispersibility in a resin during production of the LEDs.

[0097] Examples of particular suitable phosphors derived from various groups are compiled in Table 1:

[0098] Table 1

Phosphor composition

Phosphor composition	Type	Emission band peak position Ce/Eu [nm]	Composition Emission band peak position Mn [nm]
Lu3Al5O12:Ce,Mn;Si	Oxide – Garnet	525	580 – 590
CaS:Ce,Mn	Sulphide	520	580 – 620
Sr2Si5N8:Ce,Mn	Nitride	550	580 – 650
Mg2Al4Si5O18:Ce,Mn	Oxide – Alumosilicate	425	625 – 650
Mg2Al4Si5O18:Eu,Mn	Oxide – Alumosilicate	490	650 – 660
Mg2Y8(SiO4)6O2:Ce;Mn	Oxide – Oxo-orthosilicate	450	610
Ba3MgSi2O8:Eu,Mn	Oxide – Orthosilicate	450	560 – 580
MgY4Si3O13:Ce;Mn	Oxide – Oxo-orthosilicate	460	610 – 620
Ca3Sc2Si3O12:Ce,Mn	Oxide – Orthosilicate	490	690
Ca2GdZr2(AlO4)3:Ce,Mn	Oxide – Aluminate	500	590
Ba1.55Ca0.45SiO4:Eu,Mn	Oxide – Orthosilicate	500	600
BaMg2Si2O7:Ce;Mn	Oxide – Pyrosilicate	430	680 – 700
Y10(Si6O22N2)O2:Ce,Mn	Oxide – Oxynitride	430	610 – 650
Sr3Y2Ge3O12:Ce,Mn	Oxide – Orthogermanate	520	650
Ca4Si2O7F2:Ce,Mn	Oxide – Halosilicate	450	550 – 600
La9.33(SiO4)6O2:Eu,Mn	Oxide – Oxo-orthosilicate	510	580 – 620
Na2Ba6(Si2O7)(SiO4)2:Ce,Mn	Oxide – Pyrosilicate/Ortho-silicate	425	600 – 620
Ba9Sc2Si6O24:Eu,Mn	Oxide – Silicate	550	600 - 620

[0099] A particular preferred phosphor/activator composition is $Ca_{1-x-y}Mg_xSr_y)S:Ce_aMn_b$ wherein the indices have the following meanings: (x = 0.0 to 0.5; y = 0.0 to 0.5; a = 0.0001 to 0.01; and b = 0.001 – 0.05) and the sum of (x+y+a+b) adds to 1.

[00100] With respect to the activator cations applicant has found that specific coordination numbers are particular useful, that is:

- for Ce^{3+} : 6 – 12
- for Eu^{2+} : 6 – 8
- for Mn^{2+} : 6

[00101] Particularly preferred are also those primary light sources comprising said phosphors in an amount per area of said primary light source of from about 0.1 to about 1 mg/mm^2 and preferably about 0.5 mg/mm^2 and/or in an amount per volume of from about 0.5 to about 2 mg/mm^3 and preferably about 1 mg/mm^3.

[00102] Method

[00103] Another object of the present invention refers to a method for providing a cosy indoor illumination comprising the following steps:

(a) providing a white light emitting solid light source comprising or consisting of

(i-i) a primary light source

(i-ii) a luminescent layer comprising at least one phosphor that is activated by at least two cations selected from the group consisting of Ce^{3+}, Mn^{2+}, Pr^{3+} and Eu^{2+} being capable of emitting primary radiation, said luminescent layer being deposited on said primary light source, and

(i-iii) a luminescent screen capable of converting said primary radiation into radiation suitable for the addressed illumination application, and

(b) operating said solid light source at an excitation density of about 0.1 to about 100 W/mm^2, preferably about 0.5 to about 50 W/mm^2 and most preferred about 1 to about 20 W/mm^2.

[00104] Preferably said primary light source is either a semiconductor LED, a semiconductor laser diode (LD) or an organic light emitting diode (OLED). With regard to the description of these devices and their preferred embodiments reference is made to the explanations provided above, thus, no repetition is necessary.

Industrial Application

[00105] A final object of the present invention is related to the use of the light source as claimed above for indoor illumination purposes.

Examples

[00106] Example 1

[00107] The following example illustrates the present invention by means of a white LED light source comprising a 460 nm emitting (In,Ga)N die and a luminescence layer comprising CaS:CeMn as a colour converter.

[00108] CaS:Ce(0.1%)Mn(1.0%) is suspended into a silicone precursor, typically used for the packaging of InGaN LEDs. The phosphor concentration in the suspension is selected that between 10 and 300 µg of the phosphor is deposited onto the semiconductor chip having a surface area of about 1 mm^2. Finally, a catalyst is added to polymerize the silicon precursor, and the LED is sealed by a transparent plastic cap.

[00109] The emission spectra were recorded using an Edinburgh Instruments Ltd. fluorescence spectrometer equipped with a mirror optic for powder samples. The excitation source used was an Osram 450 W Xe discharge lamp.

[00110] The invention is illustrated in more detail by **Figures 1** to **4** having the following meaning:

Fig. 1: Principle of sensitizer-mediated excitation.

Fig. 2: Emission spectra of a white light emitting pcLED as function of the driving current.

Fig. 3: CIE 1931 colour point of a white LED comprising CaS:Ce(0.1%)Mn(1%) as function of the driving current.

Fig. 4: Emission spectra of CaS:Ce(0.1)Mn(x%) as function of the Mn^{2+} concentration.

Claims

1. A white light emitting solid state light source exhibiting an incandescent-like dimming behaviour which is operated at an excitation density of about 0.1 to about 100 W/mm^2, comprising or consisting of
   (a) a primary light source;
   (b) a luminescent layer capable of emitting primary radiation deposited on said primary light source, and
   (c) a luminescent screen capable of converting said primary radiation into radiation suitable for the addressed illumination application,
   wherein
   said luminescent layer comprises at least one phosphor that is activated by at least two cations selected from the group consisting of Ce^{3+}, Mn^{2+}, Pr^{3+} and Eu^{2+}.

2. The light source according to Claim 1, wherein said primary light source is either a semiconductor LED, a COB LED, a semiconductor laser diode (LD) or an organic light emitting diode (OLED).

3. The light source according to Claim 1 and/or 2 capable of emitting two emission bands.

4. The light source according to one or more of Claims 1 to 3 exhibiting increasing colour temperature by increasing driving current.

5. The light source according to one or more of Claims 1 to 4 exhibiting a shift of its colour point towards higher colour temperatures by enhancing power density.

6. The light source according to Claim 2, wherein the semiconductor is capable of emitting radiation in the blue spectral range.

7. The light source according to Claim 2 and/or 3, wherein said semiconductor is GaN or (In,Ga)N.

8. The light source according to Claim 2, wherein said OLED contains an Ir^{3+}, Pt^{2+}, or Cu^{+} emitter.

9. The light source according to one or more of Claims 1 to 8, wherein said luminescent layer is capable of emitting primary radiation in the green to red spectral range (about 500 to about 700 nm).

10. The light source according to one or more of Claims 1 to 9, wherein said luminescent layer comprises at least one phosphor that is activated by an cation pair couple selected from the group consisting of Eu^{2+}/Mn^{2+}, Ce^{3+}/Mn^{2+}, Sb^{3+}/Mn^{2+} and Pr^{3+}/Mn^{2+}.

11. The light source according to one or more of Claims 1 to 10, wherein said luminescent layer comprises at least one phosphor selected from the group consisting of oxides, nitrides, oxynitrides, sulphides, oxysulfides and their mixtures.

12. The light source according to Claim 11, wherein said phosphor contain said activator cations according to the following coordination numbers: Ce^{3+}: 6 – 12; Eu^{2+}: 6 – 8 and Mn^{2+}: 6.

13. A method for providing a cozy indoor illumination comprising the following steps:
    (a) providing a white light emitting solid light source comprising or consisting of
    (i-i) a primary light source

(i-ii) a luminescent layer comprising at least one phosphor that is activated by at least two cations selected from the group consisting of Ce^{3+}, Mn^{2+}, Pr^{3+} and Eu^{2+} being capable of emitting primary radiation, said luminescent layer being deposited on said primary light source, and

(i-iii) a luminescent screen capable of converting said primary radiation into radiation suitable for the addressed illumination application, and

(b) operating said solid light source at an excitation density of about 0.1 to about 100 W/mm^2.

14. The method according to Claim 13, wherein said primary light source is either a semiconductor LED, a semiconductor laser diode (LD) or an organic light emitting diode (OLED).

15. The use of the light source according to one or more of Claims 1 to 12 for indoor illumination purposes.

Figure 1

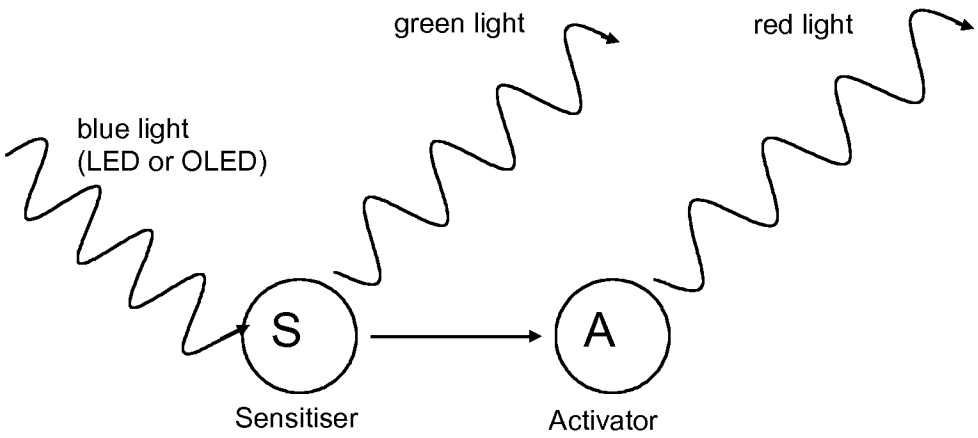


Figure 2

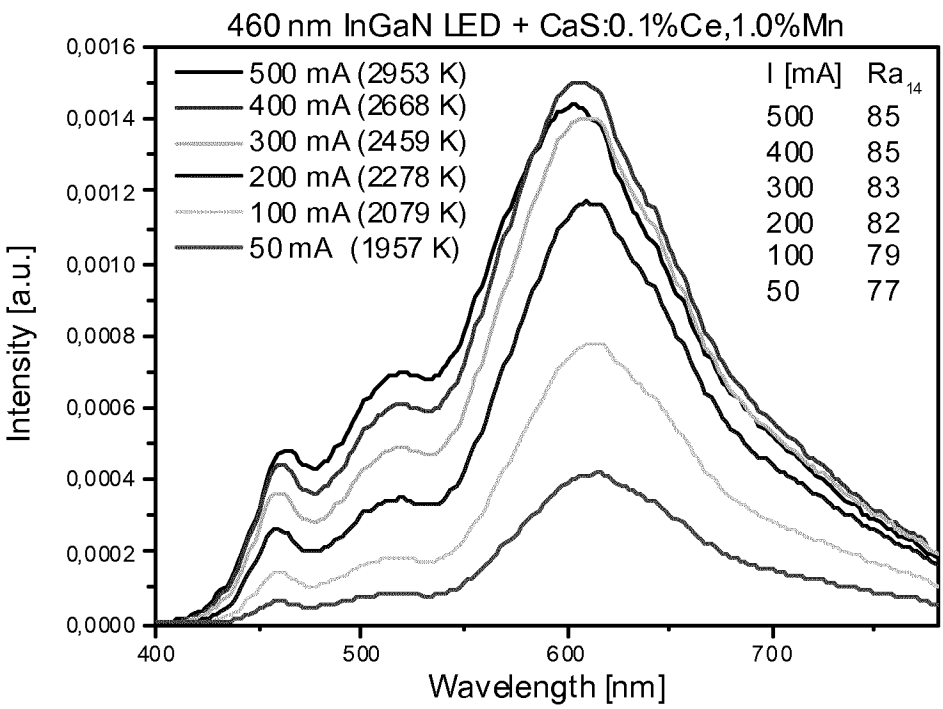


Figure 3

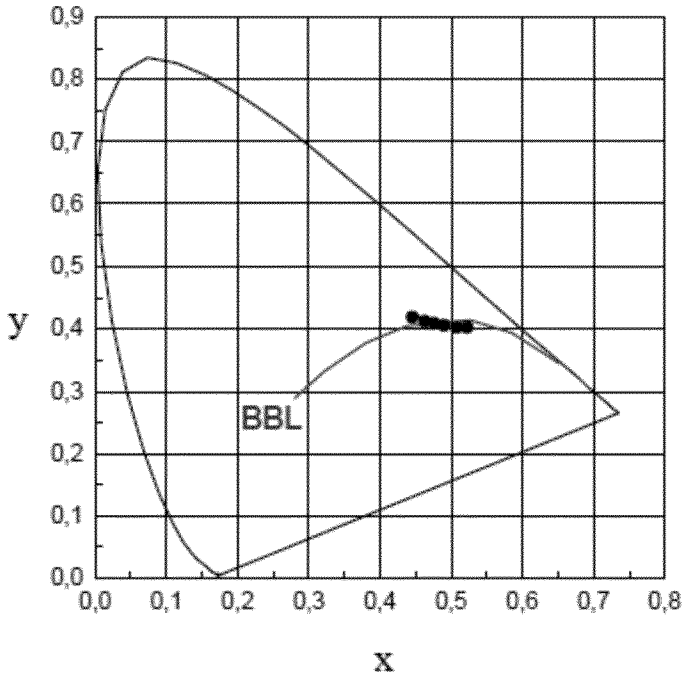
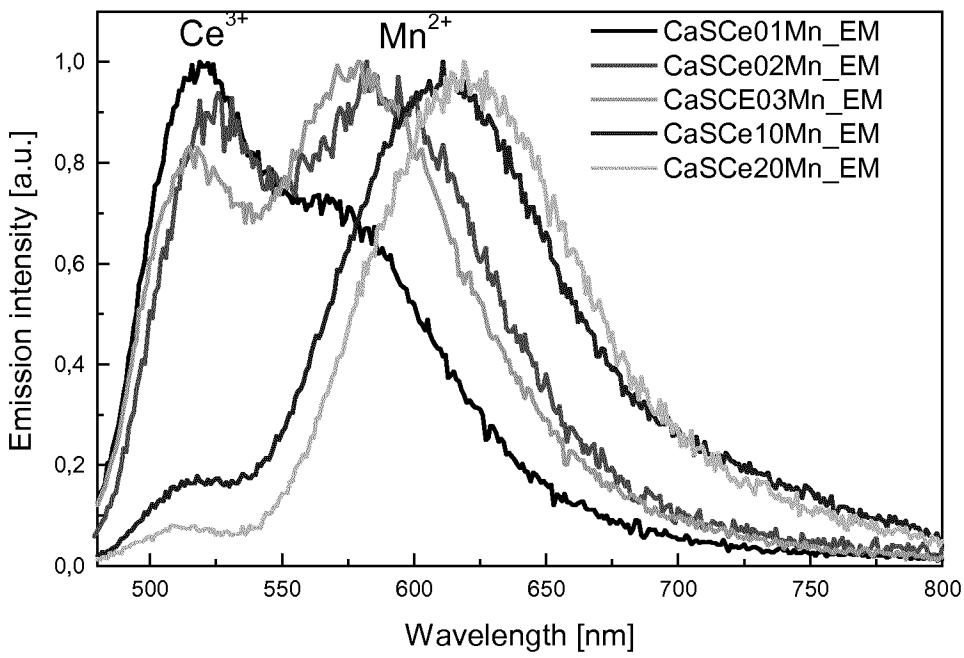


Figure 4



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/083206

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K11/77 H01J29/20
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09K H01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007/046176 A1 (BUKESOV SERGEY A [US] ET AL) 1 March 2007 (2007-03-01) paragraphs [0034] - [0038], [0061], [0168]; claims 1-45; tables 1,2 -----	1-15
X	ZIHAN XU ET AL: "Full color control and white emission from CaZnOS:Ce 3+ ,Na + ,Mn 2+ phosphors via energy transfer", JOURNAL OF MATERIALS CHEMISTRY C: MATERIALS FOR OPTICAL AND ELECTRONIC DEVICES, vol. 4, no. 41, 1 January 2016 (2016-01-01), pages 9711-9716, XP055462523, UK ISSN: 2050-7526, DOI: 10.1039/C6TC03016E paragraph [4.consclusion] ----- -/--	1-15

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

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
23 March 2018	06/04/2018

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/083206

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

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