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- (54) **Title:** WHITE LIGHT EMITTING DIODE WITH SINGLE CRYSTAL PHOSPHOR AND THE MANNER OF PRODUCTION

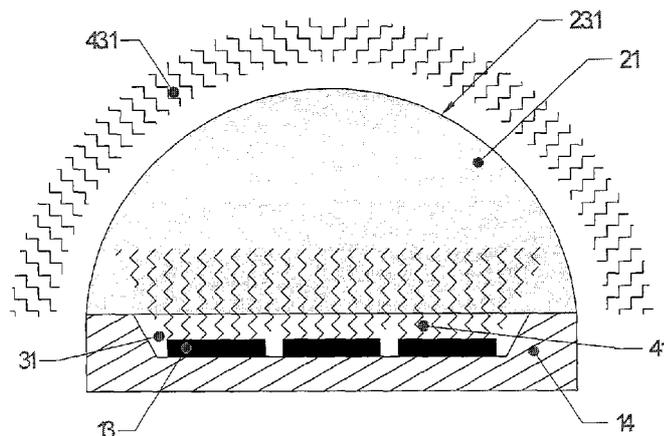
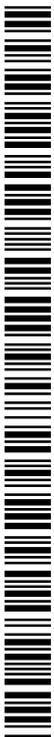


Fig. A - 2

- (57) **Abstract:** According to the invention, the diode with a single crystal phosphor placed over the chip selected from the InGaN, GaN or AlGaN group comprises the fact that the single crystal phosphor (21) is created from the monocrystalline ingot (51), created by LuYAG and/or YAP and/or GGAG masters, doped with the atoms selected from the Ce^{3+} , Ti^{3+} , C^{3+} , Eu^{2+} , Sm^{2+} , B^{3+} , C , Gd^{3+} or Ga^{3+} group, grown from the melt with the method selected from the Czochralski, HEM, Badgasarov, Kyropoulos or EFG group, when the $L_{n^{3+},y^{3+}}$ and Al^{3+} atoms can be replaced in the master up to the amount of 99.9 % with the B^{3+} , Gd^{3+} or Ga^{3+} atoms. The composition and manner of production of the phosphor (21), treatment and shape of its surface and construction of the whole diode ensure the extraction of the converted light in the direction from the InGaN chip (13) itself of the diode towards the object that is being illuminated and limit the total reflection effect on the interface of the single crystal phosphor (21) and encapsulant (31) or single crystal phosphor (21) and surrounding environment (44).



White light emitting diode with single crystal phosphor and the manner of production

Background of the Invention

The invention refers to efficient white light emitting diodes with the power above 0.5 W and luminous flux above 40 lm when utilizing the phosphor technology to convert light. Furthermore, the invention involves the optimizing of the single crystal phosphor, its composition and shape, its production technology and diode construction arrangement.

Description of Prior Art

The structure of the standard white light emitting diodes (also only as "W-LED") does not allow to emit the white light directly but is based on composing the blue (450 to 470 nm maximally) and the yellow (550 nm maximally), or, possibly, the red component of the colour spectrum (EP0936682 and US6600175 patents). In the most common arrangement, it is the structure with an InGaN chip with quantum holes, emitting blue light with emission peak between 455 to 470 nm, when quantum efficiency of the chip decreases towards the longer wavelengths and with the increasing portion of InN in the chip. The yellow component is obtained with a partial downconversion of the blue light emitted by the chip with the aid of fluorescent material that is called "phosphor". Regarding its outstanding properties, what is used in most applications as the phosphor is $(\text{Yi}_a\text{Gda})_3(\text{Ali}_b\text{Ga}_b)_5\text{O}_{12}:\text{Ce}^{3+}$, where $0 < a < 1$, $0 < b < 1$, - yttrium-aluminium garnet doped with cerium, or possibly with gallium or gadolinium (further on only as YAG.Ce). Blue light photons absorbed in this material are converted with up to 100% efficiency due to the Stokes shift into photons with lower energy and emission peak at 55 nm (EP0936682 patent). The amount of converted blue photons is directly proportionate to the Ce^{3+} atoms concentration in the material.

All these phosphors are applied over the diode in the forms of a layer of powder or poly-crystalline ceramics with the grain size of hundreds of nanometres up to tens of micrometers (US/8133461, WO/2008/051486A1). The phosphor can be placed either in a thin layer directly over the InGaN chip or can be dispersed in the epoxy or silicone optics over the chip. Of utmost importance is the even distribution of the

phosphor in dependence on the light angle of the blue light from the chip to preserve the colour homogeneity of the resulting light.

When depositing the light converting phosphor it is vital to keep the homogeneous distribution of the phosphor so that the colour temperature of light should not be dependent on the angle of the light. In all stated cases, however, the commonly used powder phosphor suffers from a range of shortcomings, such as backscattering, temperature extinction and thermal degradation.

The phenomenon of backscattering of the light on the phosphor grains of the size exceeding 500 nm causes a significant decrease in the light intensity in the desired direction. The Rayleigh scattering of light on the phosphor grains with smaller size than the light wavelength results in the deflection of the photons in various directions and back too in the undesirable direction towards the chip. If the number of these scattering centres is large, the intensity of the backscattered light is not negligible and may be in tens of percent of the total intensity. Subsequently, the backscattered light is absorbed in the individual parts of the diode and contributes to its further warming-up. This phenomenon can be reduced by decreasing the grains size to the size which is lower than the light wavelength which makes them invisible for the individual photons and the light can penetrate through them more easily. However, the decreasing size of the powders results in the drop in the conversion efficiency of the phosphor due to the increasing influence of defects on the surface of the individual grains.

A significant problem of the standard diodes is the warming-up of the chip and phosphor in the course of operation. The heat is generated by the InGaN chip itself, whose efficiency is approximately 30%, and it originates too in the phosphor during the conversion of light towards longer wavelengths during the Stokes shift. The phosphor can be locally exposed to the temperature of up to 200°C, which results in the decrease in the luminescent efficiency of the phosphor (the ratio of the absorbed blue and emitted yellow photons), this is called temperature extinction of the phosphor. The extinction shows the most with the phosphor of the smallest-size grains. The internal part of the grains is monocrystalline, however, on their surface there is a large number of defects and related surface faults of the lattice structure resulting both from the working and from the natural character of the material. These defects function as no-light emission recombination centres which significantly

decrease the conversion efficiency of the phosphor. Phosphor extinction shows with the concentration exceeding 0.5 at% Ce^{3+} in the YAG master. Larger concentrations of Ce^{3+} are used at the same time to decrease the volume of the powder phosphor and to reduce the backscattering effect.

Equally, the increased temperature significantly increases the thermal degradation of the individual parts of the diode. Silicone polymers, the most commonly used encapsulant and lens materials of efficient W-LEDs, are relatively stable. Despite of this, the thermal influence causes the encapsulant material decomposition and the creation of optically active defects on the border of the microcrystalline grain of the phosphor and encapsulant. These defects contribute to the decrease of the total radiated power and further diode warming-up.

One manner of solving the problems related to heat generation is something that is called "remote phosphor" (WO/2010/143086A1; EP2202444; WO/2012/092175A1; WO/2009/134433A3), when the converting material of the phosphor powder is dispersed onto a larger surface and located outside the direct contact with the InGaN chip. For example, it is deposited in a thin layer onto the optically permeable plate located in the blue light beam emitted by the chip or located onto the internal wall of the external lamp sheath so that at least some portion of the blue light is converted towards the longer wavelengths.

The solution to the major drawbacks of powder and polycrystalline ceramic materials is the use of transparent single crystal phosphor. The monocrystalline layer also significantly decreases the scattering of light in comparison with the polycrystalline phosphor and eliminates the effect of undesirable backscattering. The patents (WO2009/126272) of the CREE company depict the use of monocrystalline layers of the $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$, $\text{Tb}_{3-x}\text{RE}_x\text{O}_{12}:\text{Ce}^{3+}$ or $\text{S}^{x-y}\text{Ba}_x\text{Ca}_y\text{SiO}_4:\text{Eu}$ phosphors, prepared by epitaxial methods or by the method of extracting the rotating crystal from the melt, both directly on the InGaN chip and on the substrate from which it is subsequently transferred above the InGaN chip. In case of the (WO2009/126272) patent the single crystal phosphor is always rigidly connected with the chip so that better outcoupling of the generated light from the chip is achieved, with the refractive index exceeding 2.4. In case of light transition directly into the single crystal phosphor with the

refractive index minimally 1.7 it is possible to obtain more light from the chip than with the commonly used encapsulant which has refractive index between 1.4 and 1.6.

The thickness of the epitaxial layer, prepared by the Liquid Phase Epitaxy (LPE) methods, is however limited by several tens of micrometers and to obtain sufficient light absorption from the chip, the layer must be strongly doped with Ce^{3+} . Due to the cerium atom size, the high doping agent concentrations result in the increased number of defects which decrease the luminescent efficiency of the resulting layer. The (WO2009/126272) patent describes too the possibility of doping the phosphor with several various doping agents in some regions over the InGaN chip itself so that the better colour rendition of the resulting white diode is achieved due to the broader colour spectrum emission.

The patent (WO 2009/126272) specifies the utilization of circular monocrystalline plates of the 0.5 to 1 mm thickness and of the 6 mm diameter as the phosphor. The phosphor surface can be cut, textured or planarised. According to the patent (WO 2009/126272), to achieve the spatially more homogeneous colour rendition, foreign particles are added in the phosphor itself or to the encapsulating material, functioning as scattering centres, however, the type of the useable material is not specified in any single example. The single crystal phosphor always at least partially covers the chip and a portion of light is converted through it.

Furthermore, this patent (WO 2009/126272) mentions the use of a single crystal on the basis of $YAG:Ce^{3+}$ as a self-supporting substrate for the preparation of semiconductor structures on the basis of InGaN which could result in the decrease in the total internal reflection in the semi-conductor chip itself with the refractive index of 2.5, which is, however, not feasible in practice due to the different lattice constant of both the materials. The difference in lattice constant of both the materials, that is 12.01 Å for single crystal YAG and 5.185 Å for GaN up to 5.69 Å for InN, will lead to a massive creation of internal defects and dislocations in the InGaN chip and to a significant deterioration of operational properties and stability.

The patent attempts to solve the application of light-converting structures on the basis of the single crystal phosphor which shows better properties than its powder variants and deals with the arrangement of chip fitting with the phosphor.

In the stated patent (US2008/0283864), the single crystal phosphor from the materials on the basis of $Y_3Al_5O_{12}$, $Ca_xSr_yMg_{1-x-y}AlSiN_3$, $Sr_{2-x}Ba_xSiO_4$, $SiAlON$, Y_2O_3 or La_2O_3 , produced from melt by the Czochralski or Bridgeman methods, is used in the form of light-converting structures with planar surfaces which is fixed onto the chip with a silicone adhesive layer. According to this patent, the single crystal phosphor with the thickness of 10 nm to $200\mu m$ achieves cerium doping in the range of 0.1 up to 20 % or 0.5 up to 20 % of europium.

Thus it proposes to adjust the phosphor shape and size so that the chip could be spatially fitted with the phosphor, the phosphor surface can be textured, roughened or shaped differently to decrease the total reflexion phenomenon. The single crystal phosphor can too be complemented with one more optical element for the better outcoupling of light from the chip.

According to this patent too, the polished single crystal phosphor can be utilized as the substrate for the semi-conductor chip production. It includes too the preparation of the single crystal phosphor layer on the semi-conductor chip itself with the method of thin layers preparation and the opposite procedure where the semi-conductor chip is prepared by growing with classical methods on a polished layer of the single crystal phosphor. Nevertheless, in both the stated cases the problem is the different value of the material lattice constant, leading during the growing process to the creation of internal defects, such as dislocations.

Summary of the Invention

According to the invention, the white light emitting diode with single crystal phosphor located over the chip selected from the InGaN, GaN or AlGaN group comprises the fact that the single crystal phosphor is created from the monocrystalline ingot (51) on the basis of the masters with the chemical composition $LuYAG$ $/(Lu,Y)_3Al_5O_{12}/$ or YAP $/YAlO_3/$ and/or $GGAG$ $/Gd_3(Al,Ga)_5O_{12}/$ doped with atoms selected from the Ce^{3+} , Ti^{3+} , Cr^{3+} , Eu^{2+} , Sm^{2+} , B^{3+} , C , Gd^{3+} or Ga^{3+} group grown from the melt with the method selected from the Czochralski, HEM, Badgararov, Kyropoulos or EFG group.

The single crystal phosphor contains masters on the basis of $(\text{Lu}_x\text{Y}_{1-x})_3\text{Al}_5\text{O}_{12}$, where X is 0.01 to 0.99 or YAlO_3 , doped with Ce^{3+} , Ti^{3+} , Cr^{3+} , Eu^{2+} , Sm^{2+} , B^{3+} , wherein the Lu^{3+} , Y^{3+} and Al^{3+} atoms are replaced in the master with the B^{3+} , Gd^{3+} or Ga^{3+} atoms in the amount of 0.01 to 99.9 wt %.

The concentration of Ce^{3+} in the single crystal phosphor ranges between 0.02 to 0.5 wt % and/or the concentration of Sm^{2+} ranges between 0.01 to 3 wt % and/or the concentration of Eu^{2+} ranges between 0.001 to 1 wt % and/or the concentration of Ti^{3+} ranges between 0.05 to wt 5% and/or the concentration of Cr^{3+} ranges between 0.01 to 2 wt %.

The single crystal phosphor preferably contains induced colour centres on oxygen vacancies with emission peaks at 410 nm and 615 nm.

The single crystal phosphor is preferably provided with minimally one more layer of a complementing phosphor on the basis of aluminates from the $(\text{Lu},\text{Y})_3\text{Al}_5\text{O}_{12}$, $\text{Y}_3\text{Al}_5\text{O}_{12}$, YAlO_3 or Al_2O_3 group, doped with rare earths.

The single crystal phosphor is preferably created with minimally one layer consisting of $(\text{Lu},\text{Y})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ with the concentration of Ce^{3+} 0.01 up to 0.5 wt % and minimally with one more layer composed of $\text{YAlO}_3:\text{Ti}^{3+}$ with the concentration of Ti^{3+} 0.1 up to 5 wt %.

The phosphor surface, averted from the chip, ensures the extraction of converted light in the direction from the diode InGaN chip itself towards the object that is being illuminated and, therefore, there are attempts to limit the total reflection effect on the interface of the single crystal phosphor and encapsulant or the single crystal phosphor and the external environment.. The following manner of phosphor treatment and the final white light emitting diode structure contribute to the limitation.

The manner of single crystal diode phosphor production in accordance with the invention consists furthermore in that that the monocrystalline ingot is cut with a diamond-charged saw into monocrystalline slabs with the width of 0.2 to 2 mm and, subsequently, the slabs are cut with a diamond disk saw or with pulse laser, water jet with abrasive or their combination into individual single crystal phosphor plates with the external side of 1 to 5 mm and are provided with grooves or cut-outs in the places of electrical chip contacting with gold or silver wire.

The monocrystalline ingot can also be cut into monocrystalline cubes with the sides of 1.5 to 10 mm. The monocrystalline cubes are subsequently worked to obtain the shape of spherical caps with the radius of 0.5 up to 5 mm, which are then located at least partially over the semi-conductor chip.

The surface of the slabs or spherical caps of the single crystal phosphor averted from the chip is roughened with scratches orientated sand blasting with Al_2O_3 , SiC, diamond with the grain size of 0.1 to 5 micrometers or is cut in the range $R_a = 0.8$ to $5 \mu\text{m}$ or is chemically and mechanically treated with HF, H_3PO_4 , $\text{H}_3\text{PO}_4 + \text{H}_2\text{SO}_4$ or $\text{HNO}_3 + \text{HCl}$ acids or is etched in the NaOH, KOH, KHSO_4 or borax melt or is plasma-etched with fluorides or bromides.

Laser, water jet with abrasive or mechanical micro-drilling creates in the monocrystalline slab scattering centres in the shape of holes with the diameter of 20 to $40 \mu\text{m}$, whose mean distance is between 50 to $300 \mu\text{m}$ and which serve as the scattering centre for converted light.

The single crystal phosphor surface in the shape of a plate or spherical cap averted from the chip is polished and, then, provided with an anti-reflex layer on the side in the direction of the extracted light.

A layer of crushed monocrystalline ingot is preferably applied in silicone encapsulant or with plasma deposition on the surface of the single crystal phosphor in the shape of a plate or spherical cap, averted from the chip.

The lateral single crystal phosphor plate edges are preferably chamfered under the 45° angle and serve as reflex surfaces for the light spontaneously emitted into the sides.

The internal surface of the single crystal phosphor in the shape of a plate or spherical cap nearer the chip is preferably polished by working with Al_2O_3 or diamond and is treated with a reflex layer for wavelengths exceeding 500 nm and the surface averted from the single crystal phosphor chip is roughened and/or provided with scattering centres in case it is in the shape of a plate.

The light emitting diode where the single crystal phosphor has the afore mentioned composition and is produced and adjusted according to the afore mentioned procedures and is in the shape of a plate or spherical cap, is fixed to the chip with transparent silicone.

The single crystal phosphor is preferably separated physically from the chip and there is a light conducting silicon layer with the refractive index of minimally 1.5 between the chip and the single crystal phosphor and the single crystal phosphor is physically connected with the cooler to optimize the withdrawal of the generated heat away from the phosphor itself.

The diode preferably contains minimally one chip and minimally one single crystal phosphor and the chips and single crystal phosphor are the same or different.

The diode can also contain minimally 2 chips and one single crystal phosphor.

The diode can contain minimally 2 chips, when minimally one chip is fitted with the single crystal phosphor according to the invention and minimally one chip emits light with the peak between 600 to 700 nm.

The single crystal phosphor on the basis of $(\text{Lu},\text{Y})\text{sAl}_{5012}:\text{Ce}$ (LuYAG:Ce) has the main absorption peak shifted up to 445 nm, in comparison with the YAG:Ce material where it is at 460 nm, in dependence on the Y and Lu atoms ratio, and is better suited for the InGaN chips emitting in this area, see Figure A-1 . It also enables to change the emitting maximum of the phosphor in the area from 535 to 555 nm, depending on the Lu and Y atoms ratio, so that the CRI value is maximized. In doing so, the conversion efficiency of the phosphor does not change at all.

In comparison with the YAG:Ce material, patented in the current patents, the utilization of the phosphor on the basis of LuYAG:Ce, emitting green light, results in better coverage of the whole visible spectrum and when combining with another phosphor for red light or with another red light source in the area above 600 it results in the colour rendition index values exceeding 95. The material also shows high thermal luminescence stability and resistance against temperature extinction, up to the 700 K temperatures.

The single crystal phosphor on the basis of $\text{Gd}_3(\text{Al},\text{Ga})\text{sO}_{12}:\text{Ce}$ (GGAG:Ce) has the main absorption maximum shifted up to the area around 440 nm thanks to which it can be combined with corresponding InGaN chips with emission peaks below 450 nm, for which the YAG:Ce material does not have sufficient absorption. Such InGaN chips are also more stable in the broader range of the through-passing flow than the chips emitting to 460 nm and show a higher quantum efficiency. The light spectrum emitted by the single crystal phosphor on the basis of $\text{Gd}_3(\text{Al},\text{Ga})_5\text{O}_{12}:\text{Ce}$ is identical with the phosphor on the basis of YAG:Ce. In combination with the red

complementing phosphor or a diode emitting in the red area it is possible to obtain light with colour rendition index CRI better than 90. When compared to the YAG material, the single crystal on the basis of GGAG has also the advantage of being more easily workable since the GGAG hardness is 7.5 in the Mohs scale of hardness and in case of the single crystal YAG it is 8.5.

The single crystal phosphor on the **YAIO₃** (YAP) master basis enables to obtain completely new phosphor kinds which cannot be efficiently produced in the powder form since the perovskite phase is less preferable compared to the garnet phase and the preparation of the pure perovskite phase in the powder form is virtually impossible. However, when preparing the material from melt, the conditions for growth can be established in such a manner that the resulting single crystal is composed of the perovskite phase only. YAP based phosphors deliver efficiencies comparable with YAG based fluorescent materials when the shifted lattice parameters of YAP compared to YAG shift the absorption and emission of most dopants for even several hundred nm, for example YAP:Ce emits light with the 370 nm peak compared to YAG:Ce with the 555 nm peak. The YAP:Ti material emits in the orange colour spectrum area with the emission peak near 580 nm and absorption in the area of 410 to 500 nm.

The significantly smaller ratio between the phosphor volume and surface in comparison with the single crystal phosphors powder versions also contributes to the significantly higher resistance of the phosphor and encapsulant interface.

The manner of single crystal phosphor production according to the invention increases the total extraction intensity of the light being extracted from the phosphor which is accomplished by limiting the total reflection influence on the interface of the single crystal phosphor and silicon polymer / epoxy optics or internal environment.

Limiting the total reflection influence and increasing the extraction intensity in the desirable direction can be accomplished in several manners. One of the options is the treatment of the single crystal phosphor surface averted from the chip in such a way that it contains surface unevennesses of the size corresponding minimally to the extracted light wavelength. The defects of a significantly smaller size than the yellow

light wavelength remain almost invisible for this light due to the influence of the light wave character, there occurs only the Rayleigh scattering.

Another option is to induce scattering centres in the material in the form of defined monocrystalline material absence, changing randomly the direction of penetrating beams, which significantly decreases the amount of total reflections inside the single crystal phosphor. The scattering centres (22) can be created with bubbles or other defined material structures inside the material, prepared during the single crystal growth phase with the EFG method, for example, or during the single crystal working. The single crystal phosphor can also function as the optics itself above one or several semi-conductor chips. For example Figure A-2, where there is no need for other silicone, epoxy or mirror optics (31) to make light homogeneous. This is accomplished by having the phosphor side averted from the chip (23.1) in the shape of the spherical cap so that the transformed light impinges on the phosphor and surrounding environment interface as near the perpendicular line as possible and increases the total extraction performance at the expense of the light, trapped in the phosphor due to the total reflection effect (43.2).

In comparison with the so far patented procedures, the material used as the single crystal phosphor is the material enabling the efficient use of the InGaN chips with the emission peak even below 460 nm which makes it possible to obtain a diode with up to 5% higher luminescent efficiency (lm/W) in comparison with the standard diodes and it covers too the visible light area below 450 nm. The phosphor is also used as the optics itself of the efficient white light emitting diode which simplifies the construction of the whole device. The single crystal phosphor with optimized external phosphor surface, averted from the chip, also delivers significantly higher external luminescent efficiency, higher ratio of the extracted light from the phosphor and of the light absorbed by the phosphor, in comparison with all the so far utilized solutions. There is too a significant decrease in the reverse light reflection causing the chip and phosphor warming-up which extends the real time of diode durability since there does not occur such intensive thermal degradation of the phosphor material itself, nor the degradation of the phosphor and silicone lens interface.

List of pictures

- A-1 Normalized YAG:Ce, LuAG:Ce and GGAG:Ce materials absorption spectra
- A-2 Light emitting diode with a single crystal phosphor
- B-1 Single crystal phosphor spherical caps production procedure
- B-2 Light emitting diode with a single crystal phosphor in the shape of spherical cap with contact openings
- B-3a Single crystal phosphor plates production procedure
- B-3b Single crystal phosphor plates with opening for chip contacting
- B-3c Single crystal phosphor plates layout on supporting foil
- B-3d Single crystal phosphor plates layout on supporting foil
- B-3e Single crystal phosphor plates layout on supporting foil
- B-3f Light emitting diode with a single crystal phosphor in the form of a plate
- B-7a Single crystal phosphor with scattering centres in the form of holes
- B-7b Light emitting diode with a single crystal phosphor with induced scattering centres in the form of holes
- B-8a Light emitting diode with a separated and cooled single crystal phosphor and anti-reflex layer
- B-8b Light emitting diode with more chips and a separated and cooled single crystal phosphor and anti-reflex layer
- B-9 Light emitting diode with more chips and a separated single crystal phosphor in the form of spherical cap
- B-10 Light emitting diode with a separated single crystal phosphor in the form of spherical cap
- B-12a Light emitting diode with a combination of more phosphors in the form of spherical caps
- B-12b Light emitting diode with a combination of more phosphors in the form of plates
- B-13 Light emitting diode with a single crystal phosphor in the form of a plate over more chips
- B-14 Light emitting diode with a single crystal phosphor and consisting of more layers

Reference signs list

- 10 White light emitting diode
- 11 Supporting pad
- 12 Reflecting mirror
- 13 Chip
- 14 Cooler
- 15 Heat conducting paste
- 16 Cathode
- 17 Anode
- 18 Wire
- 19 Metal conducting layer
- 20 Powder phosphor
- 21 Single crystal phosphor
- 21.1 Plate
- 21.2 Spherical cap
- 22 Scattering centre
- 23.1 Emitting phosphor surface (averted from chip)
- 23.2 Non-active phosphor surface (towards chip)
- 24 Supplementary chip
- 31 Silicone polymer
- 32 Anti-reflex layer
- 33 Reflex layer
- 41 Light from chip
- 42 Luminescent centre
- 43.1 Light from phosphor (in desirable direction)
- 43.2 Lost light
- 51 Monocrystalline ingot
- 52 Monocrystalline slab
- 53 Monocrystalline cubes
- 54 Supporting foil

Detailed Description of the Preferred Embodiments

Example 1 - production of half-balls (B - 1 scheme)

The melt for the preparation of the monocrystalline ingot 51 for the production of the single crystal phosphor 21 was in the stoichiometric composition of the resulting monocrystalline ingot 51 $(\text{Lu}_{0.6}\text{Y}_{0.4})_3\text{Al}_5\text{O}_{12}$ with 1 wt % of cerium oxide CeO_2 . Regarding the CeO_2 concentration in the melt and the developing monocrystalline ingot 51, the distribution coefficient is 10 to 1. The Ce^{3+} dopant concentration is then only 10% of the current Ce^{3+} concentration in the melt. This phenomenon manifests itself by the increasing Ce^{3+} concentration towards the end of the monocrystalline ingot 51 where, in case of the classical Czochralski method, it can double in

comparison to its beginning, and, equally, the concentration of microscopic and macroscopic defects increases towards the crystal end. To maintain the colour rendition of the resulting diode, the resulting shape or size of the single crystal phosphor would have to be adjusted. In case of the monocrystalline ingot 51 prepared by the method according to WO20121 10009 the ingot was prepared in the (111) orientation with the weight of 4.7 kg from the melt with the initial weight of 18 kg, whereas in this case the Ce^{3+} concentration variation was negligible in the monocrystalline ingot 51.

The monocrystalline ingot 51. was subsequently cut with a diamond disk saw into monocrystalline cubes 53 with 3 mm edges. Then they were gradually cut in grinding mills for precious stones working into a spherical shape with the diameter of 1.7 mm. The emitting surface 23.1 of the spherical caps 21.2 was worked during the production to obtain the roughness $R_a = 1 \mu m$. This achieves the homogeneous light extraction in all the directions. The 1.7 mm diameter balls were cemented en mass with wax onto a holder for working. Subsequently they were gradually cut off from one side until one half of the material was removed. The non-active surface 23.2 of the spherical caps 21.2 was polished with a diamond suspension. The holder with polished spherical caps 21.2 was transported into a steaming apparatus and the non-active surface 23.2 of the spherical caps 21.2 was subsequently provided with a reflex optic layer 33 consisting of 6 thin layers of SiO_2-TiO_2 with the total thickness of 4 micrometers. The individual spherical caps 21.2 were subsequently de-cemented in a thermal bath from the holder. The production procedure complied with the process in Figure B-1.

Example 2 - application of half-balls (Figure B - 2)

The single crystal phosphor 21 of the $Gd_3(Al_{0.4}, Ga_{0.6})Si_2:Ce^{3+}$ composition, produced from the monocrystalline ingot 51 prepared with the Kyropoulos method, was mechanically worked using the crystal working technology in compliance with Example 1 into the spherical cap 21.2 shape with the diameter of 1.4 mm. The emitting surface 23.1 of the single crystal phosphor 21 in the spherical cap 21.2 shape was worked with the median roughness value of $R_a = 0,7 \mu m$. The single crystal phosphor 21 was fixed to the InGaN chip 13 with a transparent silicone

polymer 31 with the refractive index minimally 1.5 to increase the optical outcoupling of light from the chip 13 towards the single crystal phosphor 21 and to cover the whole surface of the chip 13 (Figure B - 2). Cut-outs were created with laser in the spherical cap 21.2 in the place of contacting the cathode 16 and anode 17 of the InGaN chip 13. The non-active surface of the phosphor 23.2 was polished and provided with a reflex layer 33 on the basis of SiO₂-TiO₂ for wavelengths exceeding 500 nm. The phosphor light 43.1 extracted from the single crystal phosphor 21 was evenly directionally restricted to the angle of 180° in the direction from the chip 13 itself. The whole above described assembly of the white light emitting diode 10 was located on an aluminium cooler 14. The white light emitting diode 10 with the single crystal phosphor 21 in the shape of the spherical cap 21.1 showed excellent colour homogeneity of the resulting light, independent of the light angle. The resulting diode gave the impression of white colour with the CRI value = 80.5 and colour temperature CT = 6 230 K.

Example 3 - production of plates (Figure B - 3a)

Monocrystalline ingots 51 were prepared according to the WO201 2110009 method and in compliance with Example 1 with a (Lu_{0.5}Y_{0.5})₃Al₅O₁₂ master and 0.1 wt % Ce³⁺ concentration doping. The used basic materials were Al₂O₃ and L-U₂O₃ and Y₂O₃ in the stoichiometric ratio and with purity of minimally 99.995%, the doping was inserted with the CeO₂ cerium oxide with the volume of 1 wt % and purity 99.999%. The prepared monocrystalline ingot 51 from the Y₃Al₅O₁₂:Ce³⁺ material had its crystal beginning and end removed with a diamond disk saw. Subsequently, it was rounded around its circumference to obtain the uniform diameter of 110 nm. The rounded monocrystalline ingot 51 was fixed to the pad with epoxy and located within the space of the wire saw. It was cut with the diamond grain wire saw into slabs with the thickness of 0.15 mm. The individual slabs were subsequently boiled out in the HNO₃ and HCl acid mixture to remove the deposits of cement, cooling liquid and abrasive materials.

The monocrystalline slabs 52 were inspected and checked in crossed polarizers and under the UV discharge lamp to detect the presence of internal defects. The dopant content was checked by measuring the emission spectrums in randomly selected

slabs. Holes with the dimension of $B1=150 \mu\text{m}$ and $B2=200 \mu\text{m}$ in compliance with Figure B - 7a were drilled by pulse laser into the monocrystalline slabs 52 so that after locating the phosphor, the InGaN chip 13 itself could be contacted from above with the golden wire 18. The monocrystalline slab was subsequently placed onto the supporting foil 54 with UV-sensitive adhesive which was stretched in a frame, ensuring the positioning in the "pick-and-place" feeder of the automatic machine. Then the slabs 52 were cut with the Nd:YAG laser into plates with sides defined by the chip size ($A1= 1.1 \text{ mm}$ and $A2 = 1.1 \text{ mm}$) (Figure B - 3b). The dimensions of the holes and plates 2.1.1 can be varied, only the arrangement of the plates 2.1.1 on the supporting foil 54 depends on size of the chip 13 and the manner of its contacting. The arrangement was in accordance with Figure B - 3c in case of the chips 13 contacted in the corner or in accordance with Figures B - 3d or B - 3e in case of the chips 13 contacted in a different place of the chip 13. Arbitrary combination and number of these cut-outs, as well as the orientation of the individual plates 2.1.1, are technologically equivalent. The individual plates 2.1.1 remained rigidly fixed onto the supporting foil 54 until being illuminated with UV light which caused the degradation of the abrasive. The frame with the plates 2.1.2 was then placed into the holder with a vacuum or mechanical manipulator and the individual slabs 2.1.1 were subsequently placed with the "pick-and-place" handling automatic machine into the exactly defined position over the InGaN chip 13 so that the cut-outs in the monocrystalline plates 2.1.1 were in the positions of contacting the chip 13 with golden wires 18. The plates 2.1.1 were fixed to the chip 13 and monocrystalline supporting foil 11 with adhesive silicone polymer 31 (Figure B - 3f). The location of the plate 2.1.1 over the InGaN chip 13 and metal layer 19 on the supporting pad 11 was finalized by hardening the silicone polymer 31 at the defined temperature exceeding 70°C . The white light emitting diode 10 produced by the above described process showed excellent long-term stability of luminous flux, tested for the period of 500 hours and with the luminous flux of 60 lm which was also the value of a similar white light emitting diode with a powder phosphor, the drop in extraction was not observed in any of the cases.

Example 3.2 - production of plates with the EFG method

The monocrystalline slab 52 prepared with the EFG method with dimensions of 0.5 x 40 x 500 mm was prepared from the melt of the Lu_2O_3 , Y_2O_3 and Al_2O_3 oxides in the stoichiometric ratio $(\text{Lu}_{0.2}, \text{Y}_{0.8})_3\text{Al}_5\text{O}_{12}$ with the CeO_2 doping. The melt in a molybdenum crucible rose with the assistance of saturating agent towards the shaping die with the defined dimensions of 0.5 x 40 mm. There were grooves in regular distances at the edge and inside the die through which bubbles with the size of 10 to 50 μm were inserted evenly in the single crystal. Subsequently, the monocrystalline slab was cut with the Nd:YAG laser into individual single crystal phosphors 21 in the shape of plates 2.1.2 with the dimensions of 1 x 1 x 0.5 mm. The bubbles in the single crystal phosphor 21 function simultaneously as effective scattering centres that do not decrease the phosphor efficiency and increase the extraction of the light from the monocrystalline phosphor 21, otherwise restricted with the total reflection phenomenon at the interface of the single crystal and its surrounding.

Example 4 - monocrystalline slabs sandblasting

The monocrystalline ingot 5.1, prepared in accordance with Example 3, was cut with the diamond disk saw into monocrystalline slabs 52 with the thickness of 0.35 mm. The monocrystalline slabs 52 were consequently glued with wax to a metal pad and placed into a sand blasting chamber. The abrasive material on the basis of B_4C with the grain size from 0.2 to 5 micrometers was expanded from a nozzle under the angle of 10° and under the pressure of 5 bar. The impacting grains created orientated scratches on the phosphor slab surface, with grooves with the width given by the grain size, depth of approximately $\frac{1}{2}$ of their widths and lengths from units to hundreds of micrometers. After being de-cemented from the pad, each monocrystalline slab 52 was glued to the supporting foil 54 with an adhesive sensitive to UV light.

The monocrystalline slab 52 glued to the supporting foil 54 was subsequently cut with a diamond straight saw into plates 2.1.1 with the sides of 1.1 x 1.1 mm. The carrier with monocrystalline plates 2.1.1 was illuminated through the supporting foil 54 with ultraviolet light causing the degradation of the adhesive on the supporting foil 54 which thus enables the final handling of the individual phosphor plates 2.1.1.

Example 5 - slabs etching

The emitting surface 23.1 of the single crystal phosphor 21 was chemically treated to attack the surface layer into the depth of units of micrometers. The entry point was the monocrystalline slab 52 with the diameter of 60 mm and thickness of 0.3 mm. The monocrystalline slab 52 was heated to the temperature of 110°C and subsequently embedded into wax, spread in a thin layer on the teflon supporting foil 54. The other side of the slabs, that is the side with the phosphor 23.1 surface averted from the chip **13**, was provided with a silicone template in the shape of parallel lines with the distance of 100 μm , prepared with screen process printing. The teflon supporting foil 54 was then placed into the concentrated hydrofluoric acid solution and heated to the temperature of 60°C for the duration of 1 hour. In places which were in contact with the acid, there appeared in the monocrystalline slab 52 surface defects with the depth of up to 30 μm enabling higher outcoupling of the light from the material.

Example 6 - hydrogen bromide etching

Plasma surface etching with hydrogen bromide was applied through a selective mask in the sieve onto the surface of monocrystalline slabs 52, prepared in accordance with Example 3, which resulted in defects with the depth of up to 10 μm , defined by the mask shape. The acquired surface structures increased the extraction of light in the defined parts of the phosphor.

Example 7 - holes drilling (Figure B - 7a and B - 7b)

The plate of the single crystal phosphor 21 with the dimensions of 0.2 x 1.5 x 1.5 mm with the surface of the median roughness value $R_a = 0.45 \mu\text{m}$ was provided with defined openings with the diameter of 20 to 25 μm , prepared with laser beam drilling (Figure B - 7a). These openings then act as scattering centres 22 in the shape of holes. The monocrystalline slab 52 was inserted in the holder with linear drives under the laser head. The pulse Nd:YAG laser illuminated the monocrystalline slab 52, whilst the linear engines moved the monocrystalline slab 52 with the speed of 600 mm/min in the X axis. When the edge of the monocrystalline slab 52 was reached,

the slab was always shifted in the Y axis by $70 \mu\text{m}$ and in the counter direction in the X axis. This process was repeated until the whole monocrystalline slab 52 was provided with defined holes with the diameter of 20 to $25 \mu\text{m}$. The arrangement of scattering centres 22 in the form of holes is performed in the manner to maximize the probability of scattering of light during the passage through the phosphor. The plate 21.1 was placed over the InGaN chip 13 and the supporting pad 11 and fixed with the transparent silicone polymer 31. The light 4± coming out of the InGaN chip 13 was partially converted with the single crystal phosphor 21 during the absorption in the luminescent centre 42 and the light from the chip 41 passed partially through it. The light generated by the luminescent centre 42 in the single crystal phosphor 21 was evenly emitted in all sides. The lost light 43.2, which would be trapped in the single crystal phosphor due to the total reflection influence or would be emitted into sides, will be diverted at the scattering centres 22 and, with a higher probability, the light from the phosphor 43.1 will be extracted in the desirable direction from the emitting surface of the phosphor 23.1 (Figure B - 7b).

Example 8 - plate with anti-reflex layer + chamfering (Figures B - 8a and B - 8b)

The monocrystalline slabs 52 with the thickness of 0.5 mm were treated with the mechanical working (Example 7) or chemical and mechanical working (Example 6) on the emitting surface of the phosphor 23.1 so that the increase in light extraction from the phosphor 43.1 from the single crystal phosphor 21 was achieved. Subsequently, this surface was polished with a polishing agent with loose diamond so that the scratch/dig surface quality (according to the MIL-0-13830A standard) reached the value of minimally 40/20. Then the anti-reflex layer 32 on the basis of MgF_2 was applied with steaming on the polished surface of the slabs 52 for the wavelengths from 500 to 700 nm, which resulted in the increase in the extraction of the yellow and red components of visible light. The other side of the monocrystalline slab 52 non-active phosphor surface 23.2 was worked with abrasive materials in such a manner that the median roughness value was $R_a = 0,2 \mu\text{m}$ and was provided with a reflex layer 33 for the wavelengths exceeding 500 nm. The plate 21.1 of the single crystal phosphor 21 was subsequently produced in such a manner that its edges were chamfered with facets in the angle of 45° . This was acquired by cutting

the monocrystalline slab 52 with a diamond disk saw with the chamfering of 45°. In the application the plate 21.1 was placed into the cooler 14 (as the "remote phosphor") and connected with it thermally with a heat-conducting paste 15 over one (Figure B - 8a), or, possible, over more individually controlled chips 13 (Figure B - 8b). The facets served equally as scattering surfaces for lost light 43.2 which would otherwise have spread into the sides. The space between the chip 13, cooler 14 and plate 21.1, through which the light from the chip 4.1 passed, was filled up with the transparent silicone polymer 3.1 with a refractive index of 1.5.

Example 9 - remote half-ball over more chips (Figure B - 9)

The monocrystalline material of the phosphor 21 was worked into the spherical cap 21.2 with the radius of 5 mm, in accordance with Example 1. The single crystal phosphor 21 was subsequently fitted into the alumina cooler 14 over four InGaN chips 13 emitting blue light. During the passage through the single crystal phosphor 21 in the luminescent centres 42, the light from the chip 4.1 is converted with the Stokes shift. The emitting phosphor surface 23.1 was polished in the quality $R_a < 0.1 \mu\text{m}$. The single crystal phosphor 21 was connected to the alumina cooler 14 with heat-conducting paste 15. The transparent silicone polymer 3.1 with the refractive index of minimally 1.5 was used as the light conducting layer between the spherical cap 21.2 and the individual chips 13. In this arrangement, more than 50 % of the converted light from the phosphor 43.1 was emitted in the desirable direction by the emitting surface 23 in the direction away from the chip 13.

Example 10 - spherical cap and reflex layer (Figure B - 10)

The single crystal phosphor 21 in the shape of the spherical cap 21.2, prepared in accordance with Example 1, was placed over the chip 13 and separated ("remote phosphor") with silicone polymer 3.1 which served as a light-conducting layer for the light generated by the chip 4.1. The single crystal phosphor 21 was placed in such a position that it would be in physical contact with the cooler 14. To improve the transfer of the heat generated by the single crystal phosphor 21, it was connected with the thermal cooler 14 with the heat-conducting paste 15. In this manner it is possible to keep the real temperature of the single crystal phosphor 21 at the temperature of approximately 90 °C. To increase the extraction of the light from the

phosphor 43.1, the non-active surface of the phosphor 23.2 was provided with a reflex layer 33 on the basis of the $\text{SiO}_2\text{-TiO}_2$ layers, optimized for the wavelengths from 500 to 700 nm.

Example 11 - remote phosphor plate

The plate 21.2 of the single crystal phosphor 21 of a circular shape with the diameter of 2 mm and the thickness of 250 micrometres, produced from the monocrystalline slab 52 by cutting with the Nd:YAG laser, was placed in the alumina holder 14 over the InGaN chip 13. The holder functioned too as a thermal cooler 14 for the withdrawal of the heat, generated by the single crystal phosphor 21 during the conversion of the light. The single crystal phosphor 21 was connected with the thermal cooler 14 with the heat-conducting paste 15. The space between the single crystal phosphor 21 and the InGaN chip 13 was filled with the light-conducting layer of the optically transparent silicone polymer 3_1 with the refractive index of minimally 1.5.

Example 12 - more phosphors and more chips combination (Figure B - 12a and Figure B - 12b)

In the case of the diode with more InGaN chips 13, there were used several single crystal phosphors 21 ($(\text{Lu}_{0.3}\text{,Yo,7})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ with luminescence peak at 545 nm) and complementary phosphors 24 ($\text{YAlO}_3:\text{Ti}^{3+}$ with luminescence peak at 580 nm). The spherical caps 21.2 from the single crystal phosphor 21 and complementary phosphor 24 were placed directly onto the semi-conductor InGaN chip 13 (Figure B - 12a) with the emission peak at 450 nm. This resulted in acquiring the light containing the blue, yellow and red components of visible spectrum which brought a significant improvement in colour rendition. The individual single crystal phosphors 21 and complementary phosphors 24 were fixed in positions over the chips 13 on the cooler 14 with transparent silicone polymer 31. In this case, more than 50% of converted light from phosphors 43.1 is illuminated in the desirable direction. An equivalent solution may also include the combination of several InGaN chips with or only with AlGaN chips 13 emitting in the ultraviolet area or the chips emitting with the emission peak in the red area exceeding 600 nm. The equivalent solution includes too the replacement of spherical caps 23.2 with monocrystalline plates 23.1 (Figure B - 12b).

The white light emitting diode 10 in the above described arrangement provided excellent colour homogeneity of light and the colour rendition index (CRI) value equal to 85.

Example 13 - plate over more chips (Figure B - 13)

The monocrystalline plate 21.2 of the single crystal phosphor 21 with the diameter of 5 mm and thickness of 250 μm was placed over four InGaN chips 13 so that it covered all these chips. The blue light from the chip 41 passed through the single crystal phosphor 21 and was partially converted to acquire the resulting white light with the temperature of 5500 K. The plate 21.2 was fixed to the InGaN chips 13 and to the alumina cooler 14 with optically transparent silicone polymer 31.

Example 14 - sandwich (Figure B - 14)

The monocrystalline slabs 52 on the basis of $(\text{Lu}_{0.7}, \text{Y}_{0.3})_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ were used as pads for another function layer of $\text{Al}_2\text{O}_3:\text{Cr}$. This top layer of red complementary phosphor 24 was prepared with the method of the "LPE" liquid epitaxy. This layer functioned as an efficient layer for light outcoupling from the single crystal phosphor 21 and also contained a conversion phosphor with emission peak at 580 nm. The yellow single crystal phosphor 21 and the red complementary single crystal phosphor 21 were simultaneously separated in this manner to prevent the mutual undesirable dopant mixing which would lead to the increase in the total conversion material efficiency.

The same result was acquired also in the case when the second layer of the complementary phosphor 24 on the monocrystalline pad on the basis of $\text{Y}_3\text{Al}_5\text{O}_{12}$ was polycrystalline and prepared with the plasma spraying technology. The light from the chip 4.1 and the light from the phosphor 43.1 transferred without reflection directly into the material with a similar refractive index and due to a random grain orientation of this material it was outcoupled more easily from the phosphor. Silicon polymer 3.1, which functions too as the light homogenizing optics and a protective layer, was used

to fix the combined single crystal phosphor 21 and the complementary phosphor 24 over the InGaN chip 13 and the alumina cooler 14.

Example 15 - sandwich - red phosphor in silicone

The monocrystalline slab 52 on the basis of $(\text{Lu}_{0,7}, \text{Y}_{0,3})\text{3Al}_5\text{O}_{12}:\text{Ce}^{3+}$ with the diameter of 120 mm and thickness of 0.3 mm was provided from one side with a layer of $\text{YAlO}_3:\text{Ti}^{3+}$ from a crushed monocrystalline ingot 51 in an optically transparent silicone polymer 31 with the thickness of 0.2 mm. After hardening the top silicone layer, the slab was cut into the individual phosphors. To fix the combined single crystal phosphor 21 and the complementary phosphor 24 over the InGaN chip 13 and alumina cooler 14, the silicone polymer 31 was used which serves too as the light homogenizing optics and a protective layer.

Example 16 - UV phosphor with induced colour centres

The single crystal phosphor 21 on the basis of the $(\text{Lu}_{0,i}, \text{Y}_{0,9})\text{3Al}_5\text{O}_{12}$ material with induced colour centres in the places of oxygen vacancies has an intensive absorption at 370 nm. When combined with the AlGaN chip, the single crystal phosphor 21 emitted light in the whole area of visible spectrum with two main peaks at 410 and 615 nm. The resulting light gave the impression of white colour with thermal temperature $\text{CT} = 3280$ K and with the colour rendition index CRI value = 90. In case of doping the material with cerium, the emitted light achieved the colour temperature $\text{CT} = 3750$ K and the colour rendition index CRI value = 94. When excited with the ultraviolet light with emission peak of 370 nm, the undoped material LuAG in the form of single crystal phosphor emitted orange light in the area from 500 to 700 nm with emission peak at 580 nm.

Industrial Applicability

The efficient white light emitting diode (W-LED) with a single crystal phosphor can be utilized in all applications that require intensive lighting, such as the lighting of industrial halls, stadiums, street lightening, in headlights for transport vehicles, efficient personal flashlights or projectors.

PATENT CLAIMS

1. A white-light emitting diode with a single crystal phosphor placed over the chip selected from the InGaN, GaN or AlGaN group, wherein the single crystal phosphor (21) is created from the monocrystalline ingot (51) on the basis of masters of LuYAG and/or YAP and/or GGAG doped with atoms selected from the Ce^{3+} , Ti^{3+} , Cr^{3+} , Eu^{2+} , Sm^{2+} , B^{3+} , C, Gd^{3+} or Ga^{3+} group, grown from the melt with a method selected from the Czochralski, HEM, Badgasarov, Kyropoulos or EFG group.
2. The diode according to Claim 1, **wherein** the single crystal phosphor (21) on the basis of masters corresponding to a chemical formula $(Lu_x, Y_{1-x})_3Al_5O_{12}$, where X is 0.01 up to 0.99, or $YAlO_3$ doped with Ce^{3+} , Ti^{3+} , Cr^{3+} , Eu^{2+} , Sm^{2+} , B^{3+} , when the Lu^{3+} , Y^{3+} and Al^{3+} atoms are replaced in the master with the B^{3+} , Gd^{3+} or Ga^{3+} atoms in the amount of 0.1 to 99.9 wt%.
3. The diode according to Claims 1 and 2, **wherein** the Ce^{3+} concentration in the **single crystal phosphor (21)** ranges from 0.02 up to 0.5 wt % and/or the Sm^{2+} concentration ranges from 0.01 up to 0.3 wt % and/or the Eu^{2+} concentration ranges from 0.001 up to 1 wt % and/or the Ti^{3+} concentration ranges from 0.05 up to 5 wt % and/or the Cr^{3+} concentration ranges from 0.01 up to 2 wt %.
4. The diode pursuant to Claims 1 to 3 **wherein** the single crystal phosphor (21) contains induced colour centres on oxygen vacancies with emission peaks at 410 nm and 615 nm.
5. The diode pursuant to Claims 1 to 3 **wherein** the single crystal phosphor (21) is provided with minimally one more layer of the complementary phosphor (24) on the aluminate basis from the $(Lu, Y)_3Al_5O_{12}$, $Y_3Al_5O_{12}$, $YAlO_3$ or Al_2O_3 group, doped with rare earths.
6. The diode pursuant to Claims 1 to 3 **wherein** the single crystal phosphor (21) is created with minimally one layer composed of $(Lu, Y)_3Al_5O_{12}:Ce^{3+}$ with the Ce^{3+} concentration from 0.01 to 0.5 wt % and with minimally one more layer composed of $YAlO_3:Ti^{3+}$ with Ti^{3+} concentration from 0.1 to 5 wt %.
7. The manner of production of the single crystal diode phosphor according to Claims 1 to 6, **wherein** the monocrystalline ingot (51) is cut with a diamond-charged saw into monocrystalline slabs (52) with the thickness of 0.2 to 2 mm, which are subsequently cut with a diamond disk saw or pulse laser, water jet with abrasive or their

combination into individual plates (21 .1) of the single crystal phosphor (21) with the external sides from 1 to 5 mm and are provided with grooves or cut-outs in the place of electrical contacting of the chips with a gold or silver wire (18).

8. The manner of production of the single crystal diode phosphor according to Claims 1 to 6, **wherein** the monocrystalline ingot (51) is cut into monocrystalline cubes (53) with the sides of 1.5 to 10 mm, which are subsequently worked into the shape of spherical caps (21 .2) with the radius of 0.5 to 5 mm and are located at least partially over the semi-conductor chip (13).

9. The manner of production of the single crystal phosphor according to Claims 7 and 8, **wherein** the surface of slabs (52) or spherical caps (21 .2) of the single crystal phosphor (21) averted from the chip (13) is roughened with scratches orientated sand blasting with Al_2O_3 , SiC, diamond with the grain size of 0.1 to 5 micrometers or is cut in the range $R_a = 0.8$ to $5 \mu\text{m}$ or is chemically and mechanically treated with HF, H_3PO_4 , $\text{H}_3\text{PO}_4 + \text{H}_2\text{SO}_4$ or $\text{HNO}_3 + \text{HCl}$ acids or is etched in the NaOH, KOH, KHSO_4 or borax melt or is plasma-etched with fluorides or bromides.

10. The manner of production of the single crystal diode phosphor according to Claims 1 to 6, **wherein** the monocrystalline ingot (51) is cut with a diamond-charged saw into monocrystalline slabs (52) with the thickness of 0.2 to 2 mm, into which laser, water jet with abrasive or mechanical micro-drilling integrates scattering centres (22) in the shape of holes with the diameter of 20 to $40 \mu\text{m}$, whose mean distance is minimally $40 \mu\text{m}$.

11. The manner of production of the single crystal phosphor according to Claims 7 and 8, **wherein** the surface (23) of the single crystal phosphor (21) in the shape of a plate (21 .1) or spherical cap (21 .2) averted from the chip (13) is polished and then provided with an anti-reflex layer (32) on the side in the direction of the extracted light.

12. The manner of production of the single crystal phosphor according to Claims 7 and 8, **wherein** a layer of crushed monocrystalline ingot is applied in silicone encapsulant or with plasma deposition on the surface (23) of the single crystal phosphor (21) in the shape of a plate (21 .1) or spherical cap (21 .2), averted from the chip (13).

13. The manner of production of the single crystal phosphor according to Claim 7, **wherein** the lateral edges of the plate (21 .1) of the single crystal phosphor (21) are chamfered under the 45° angle and serve as reflex surfaces for the light spontaneously emitted into the sides.

14. The manner of production of the single crystal phosphor according to Claims 7 and 8, **wherein** the internal surface (23.1) of the single crystal phosphor (21) in the shape of a plate (21 .1) or a spherical cap (21 .2) nearer the chip (13) is polished by working with Al_2O_3 or diamond and is provided with a reflex layer (33) for the wavelengths exceeding 500 nm and in case the surface (23) averted from the chip (13) of the single crystal phosphor (21) is in the shape of a plate (21 .2), it is roughened and/or provided with scattering centres (22).

15. The white light emitting diode pursuant to Claims 1 and 6, **wherein** the single crystal phosphor (21) in the shape of a plate (21 .2) or a spherical cap (21 .2) is fixed to the chip (13) with transparent silicone (31).

16. The white light emitting diode pursuant to Claims 1 and 6, **wherein** the single crystal phosphor (21) is physically separated from the chip (13) and that there is between the chip (13) and the single crystal phosphor (21) a light-conducting silicone layer (31) with the refractive index minimally 1.5 and the single crystal phosphor (21) is physically connected with the cooler (14).

17. The white light emitting diode pursuant to Claims 1 to 6, **wherein** it contains minimally one chip (13) and minimally one single crystal phosphor (21) and the chips (13) and single crystal phosphor (21) are the same or different.

18. The white light emitting diode pursuant to Claims 1 to 6, **wherein** it contains minimally 2 chips (13) and one single crystal phosphor (21).

19. The white light emitting diode pursuant to Claims 1 to 6, **wherein** it contains 2 chips (13), when minimally one chip is fitted with the single crystal phosphor (21) and minimally one chip emits light with the maximum between 600 to 700 nm.

AMENDED CLAIMS

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Amended claims

1. A white-light emitting diode with a single crystal phosphor placed over the chip selected from the InGaN, GaN or AlGaN group, wherein the single crystal phosphor (21) is on the basis of hosts of LuYAG and/or YAP and/or GGAG doped with atoms selected from the Ce³⁺, Ti³⁺, Cr³⁺, Eu²⁺, Sm²⁺, B³⁺, C, Gd³⁺ or Ga³⁺ group..
2. The diode according to Claim 1, **wherein** the single crystal phosphor (21) on the basis of **hosts** corresponding to a chemical formula (Lu_xY_{1-x})₃Al₅O₁₂, where X is 0.01 up to 0.99, or YAlO₃ doped with Ce³⁺, Ti³⁺, Cr³⁺, Eu²⁺, Sm²⁺, B³⁺, **where** the Lu³⁺, Y³⁺ and Al³⁺ atoms are replaced in the **host** with the B³⁺, Gd³⁺ or Ga³⁺ atoms in the amount of 0.1 to 99.9 wt%.
3. The diode according to Claims 1 and 2, **wherein** the Ce³⁺ concentration in the single crystal phosphor (21) ranges from 0.02 up to 0.5 wt % and/or the Sm²⁺ concentration ranges from 0.01 up to 0.3 wt % and/or the Eu²⁺ concentration ranges from 0.001 up to 1 wt % and/or the Ti³⁺ concentration ranges from 0.05 up to 5 wt % and/or the Cr³⁺ concentration ranges from 0.01 up to 2 wt %.
4. The diode pursuant to Claims 1 to 3 **wherein** the single crystal phosphor (21) contains induced colour centres on oxygen vacancies with emission peaks at 410 nm and 615 nm.
5. The diode pursuant to Claims 1 to 3 **wherein** the single crystal phosphor (21) is provided with minimally one more layer of the complementary phosphor (24) on the aluminate basis from the (Lu,Y)₃Al₅O₁₂, Y₃Al₅O₁₂, YAlO₃ or Al₂O₃ group, doped with rare earths.
6. The diode pursuant to Claims 1 to 3 **wherein** the single crystal phosphor (21) is created with minimally one layer composed of (Lu,Y)₃Al₅O₁₂:Ce³⁺ with the Ce³⁺ concentration from 0.01 to 0.5 wt % and with minimally one more layer composed of YAlO₃:Ti³⁺ with Ti³⁺ concentration from 0.1 to 5 wt %.
7. The manner of production of the single crystal diode phosphor according to Claims 1 to 6, **wherein the single crystal phosphor (21) is created from the monocrystalline ingot (51) grown from the melt with a method selected from the Czochralski, HEM, Badgasarov, Kyropoulos or EFG group and is cut with a**

diamond-charged saw into monocrystalline slabs (52) with the thickness of 0.2 to 2 mm, which are subsequently cut with a diamond disk saw or pulse laser, water jet with abrasive or their combination into individual plates (21 .1) of the single crystal phosphor (21) with the external sides from 1 to 5 mm and are provided with grooves or cut-outs in the place of electrical contacting of the chips with a gold or silver wire (18).

8. The manner of production of the single crystal diode phosphor according to Claims 1 to 6, **wherein the single crystal phosphor (21) is created from the monocrystalline ingot (51) grown from the melt with a method selected from the Czochralski, HEM, Badgasarov, Kyropoulos or EFG group and then is cut into monocrystalline cubes (53) with the sides of 1.5 to 10 mm, which are subsequently worked into the shape of spherical caps (21 .2) with the radius of 0.5 to 5 mm and are located at least partially over the semi-conductor chip (13).**

9. The manner of production of the single crystal phosphor according to Claims 7 and 8, **wherein** the surface of slabs (52) or spherical caps (21 .2) of the single crystal phosphor (21) averted from the chip (13) is roughened with scratches orientated sand blasting with Al_2O_3 , SiC, diamond with the grain size of 0.1 to 5 micrometers or is cut in the range $R_a = 0.8$ to $5 \mu m$ or is chemically and mechanically treated with HF, H_3PO_4 , $H_3PO_4 + H_2SO_4$ or $HNO_3 + HCl$ acids or is etched in the NaOH, KOH, $KHSO_4$ or borax melt or is plasma-etched with fluorides or bromides.

10. The manner of production of the single crystal diode phosphor according to Claims 1 to 6, **wherein** the monocrystalline ingot (51) is cut with a diamond-charged saw into monocrystalline slabs (52) with the thickness of 0.2 to 2 mm, into which laser, water jet with abrasive or mechanical micro-drilling integrates scattering centres (22) in the shape of holes with the diameter of 20 to $40 \mu m$, whose mean distance is minimally $40 \mu m$.

11. The manner of production of the single crystal phosphor according to Claims 7 and 8, **wherein** the surface (23) of the single crystal phosphor (21) in the shape of a plate (21.1) or spherical cap (21 .2) averted from the chip (13) is polished and then provided with an anti-reflex layer (32) on the side in the direction of the extracted light.

12. The manner of production of the single crystal phosphor according to Claims 7 and 8, **wherein** a layer of crushed monocrystalline ingot is applied in silicone encapsulant

or with plasma deposition on the surface (23) of the single crystal phosphor (21) in the shape of a plate (21 .1) or spherical cap (21 .2), averted from the chip (13).

13. The manner of production of the single crystal phosphor according to Claim 7, **wherein** the lateral edges of the plate (21 .1) of the single crystal phosphor (21) are chamfered under the 45° angle and serve as reflex surfaces for the light spontaneously emitted into the sides.

14. The manner of production of the single crystal phosphor according to Claims 7 and 8, **wherein** the internal surface (23.1) of the single crystal phosphor (21) in the shape of a plate (21 .1) or a spherical cap (21 .2) nearer the chip (13) is polished by working with **Al₂O₃** or diamond and is provided with a reflex layer (33) for the wavelengths exceeding 500 nm and in case the surface (23) averted from the chip (13) of the single crystal phosphor (21) is in the shape of a plate (21 .2), it is roughened and/or provided with scattering centres (22).

15. The white light emitting diode pursuant to Claims 1 and 6, **wherein** the single crystal phosphor (21) in the shape of a plate (21 .2) or a spherical cap (21 .2) is fixed to the chip (13) with transparent silicone (31).

16. The white light emitting diode pursuant to Claims 1 and 6, **wherein** the single crystal phosphor (21) is physically separated from the chip (13) and that there is between the chip (13) and the single crystal phosphor (21) a light-conducting silicone layer (31) with the refractive index minimally 1.5 and the single crystal phosphor (21) is physically connected with the cooler (14).

17. The white light emitting diode pursuant to Claims 1 to 6, **wherein** it contains minimally one chip (13) and minimally one single crystal phosphor (21) and the chips (13) and single crystal phosphor (21) are the same or different.

18. The white light emitting diode pursuant to Claims 1 to 6, **wherein** it contains minimally 2 chips (13) and one single crystal phosphor (21).

19. The white light emitting diode pursuant to Claims 1 to 6, **wherein** it contains 2 chips (13), when minimally one chip is fitted with the single crystal phosphor (21) and minimally one chip emits light with the maximum between 600 to 700 nm.

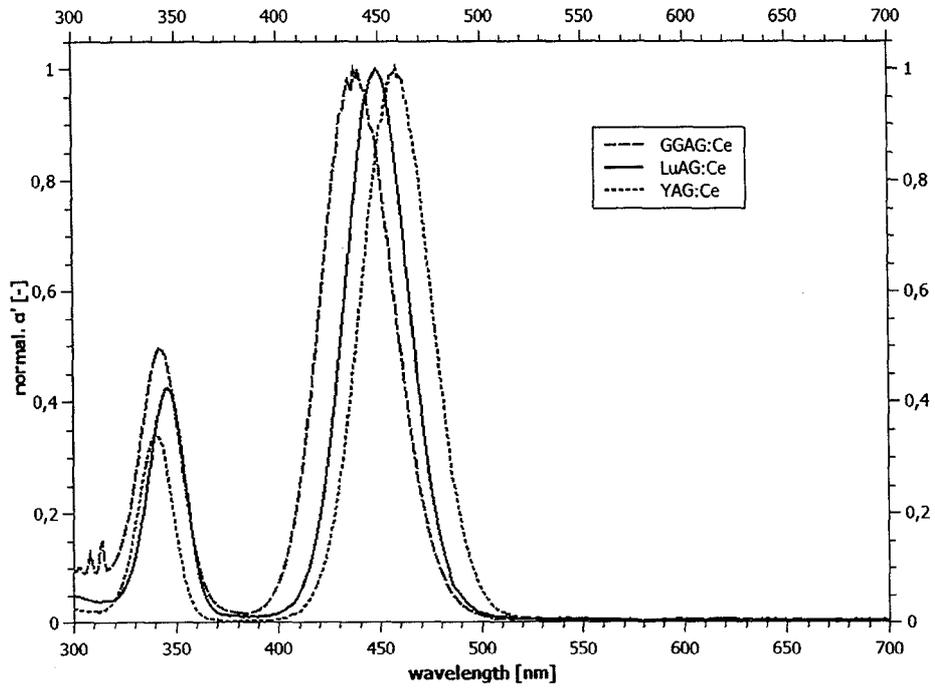


Fig. A - 1

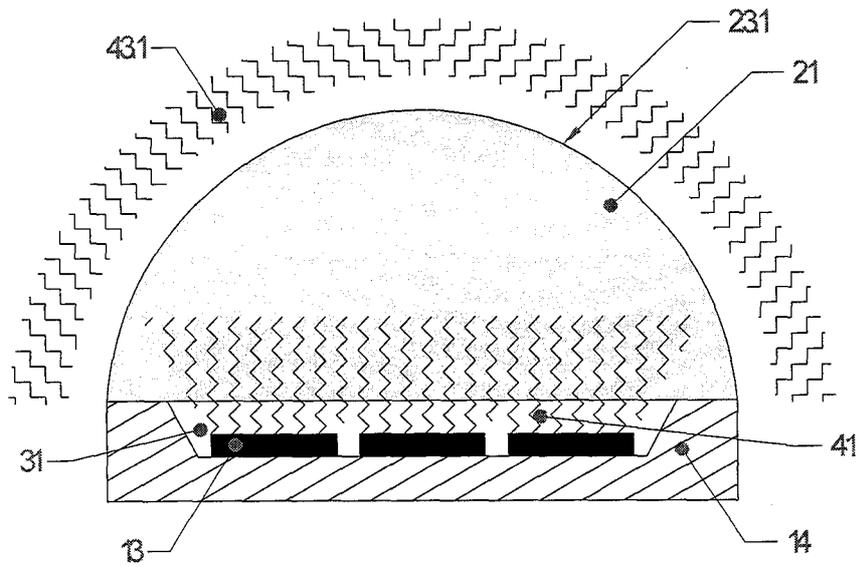


Fig. A - 2

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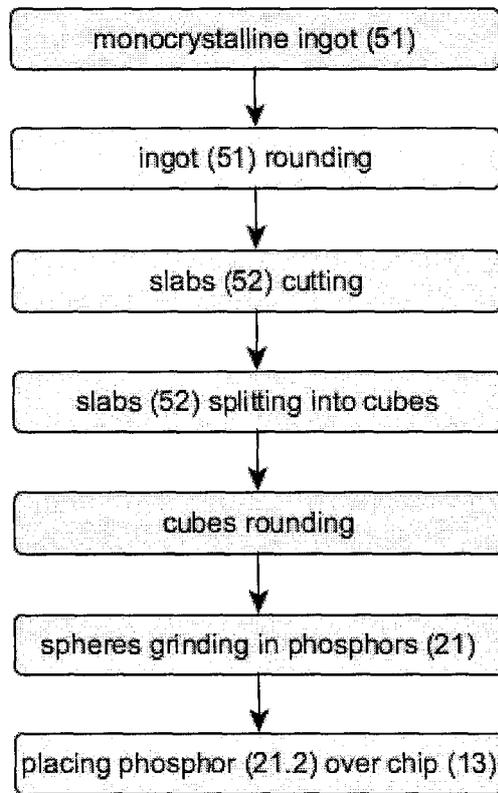


Fig. B - 1

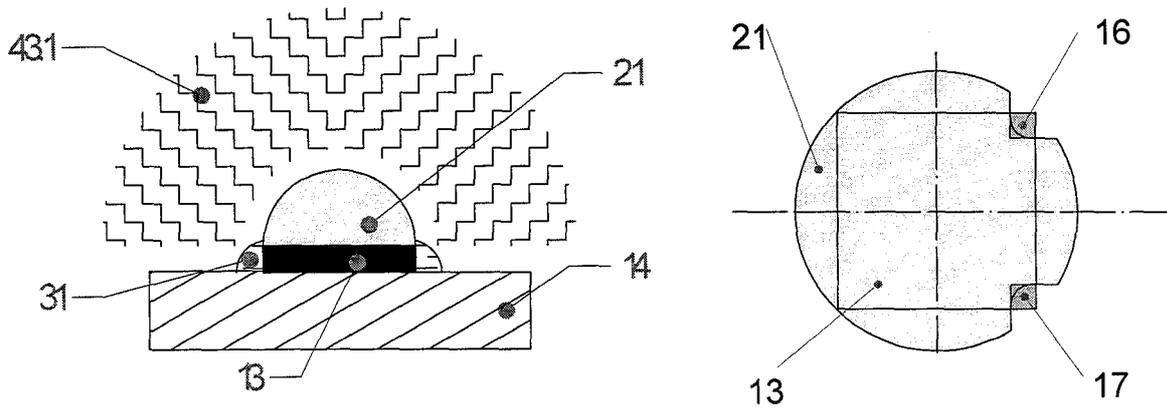


Fig. B - 2

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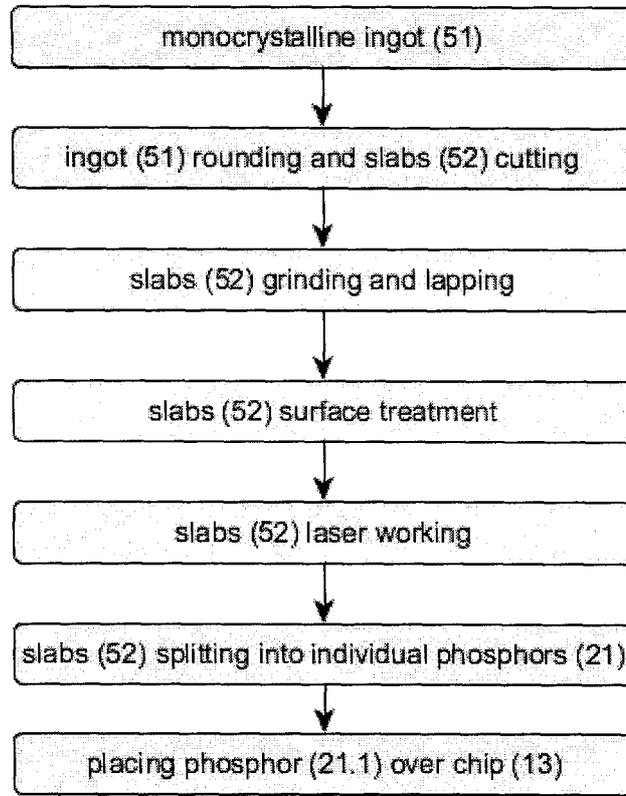


Fig. B - 3a

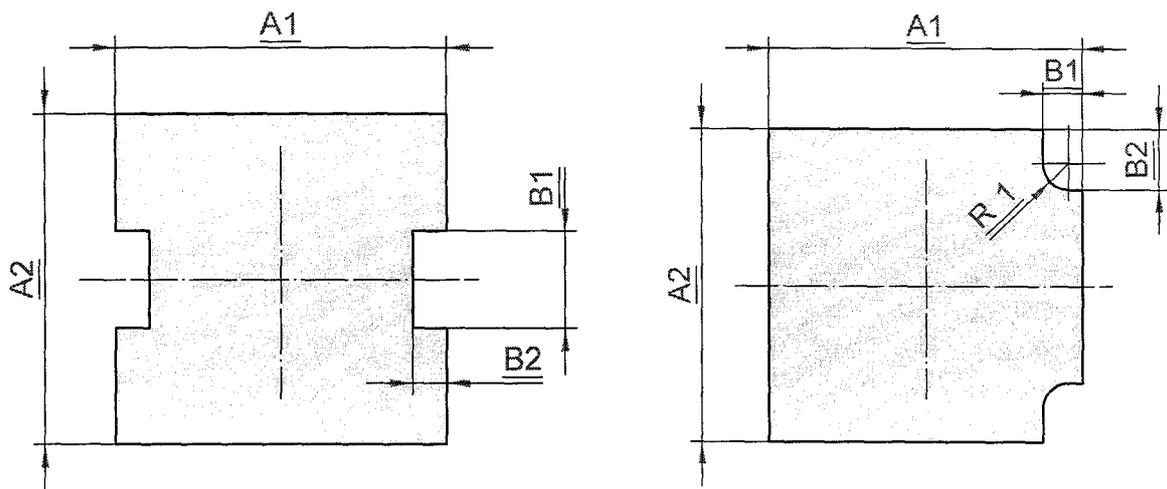


Fig. B - 3b

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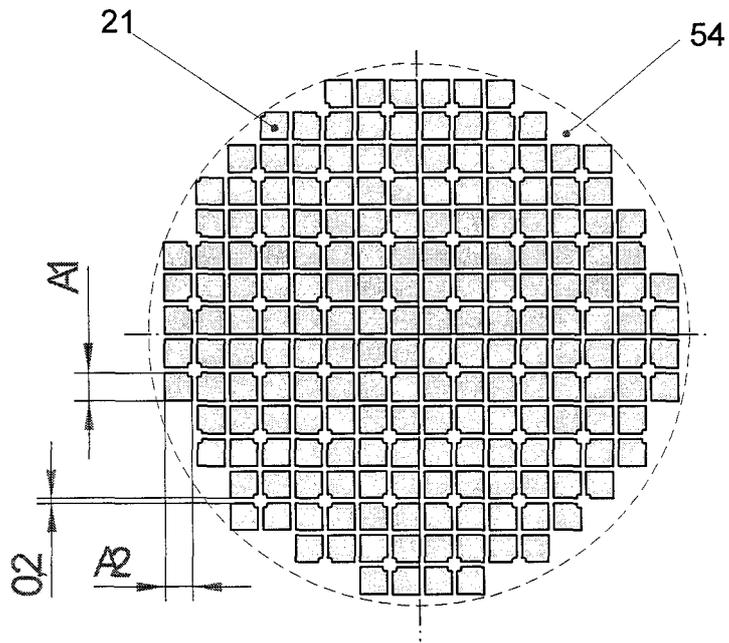


Fig. B - 3c

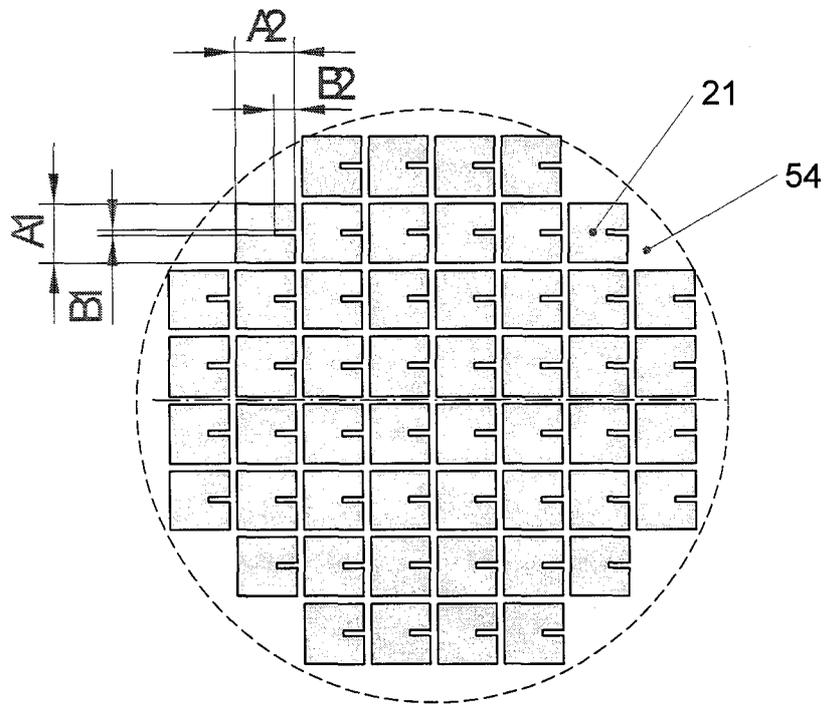


Fig. B - 3d

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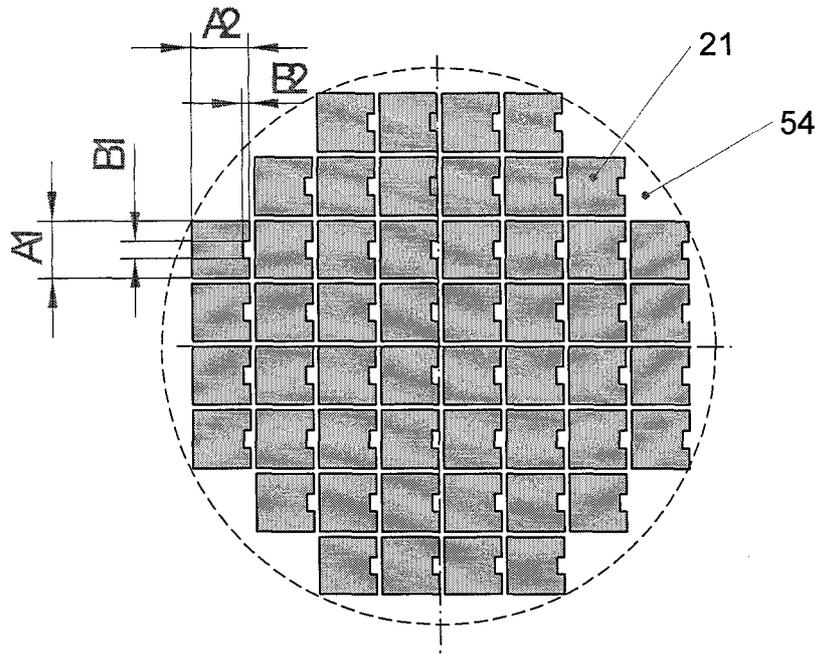


Fig. B - 3e

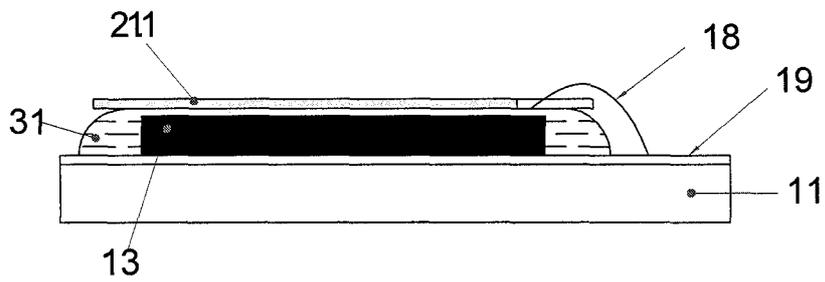


Fig. B - 3f

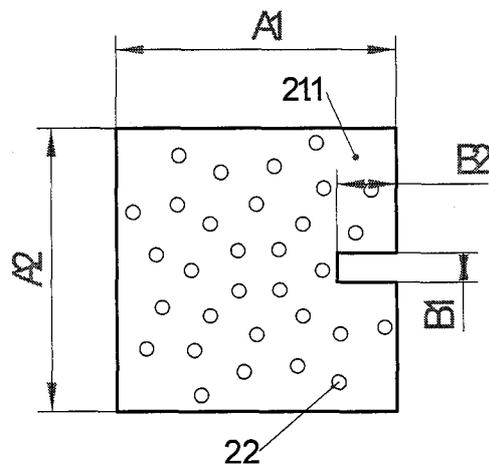


Fig. B - 7a

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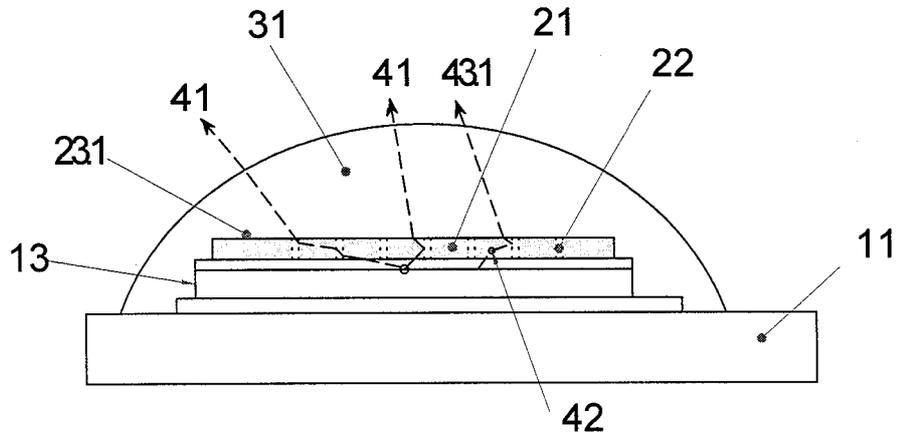


Fig. B - 7b

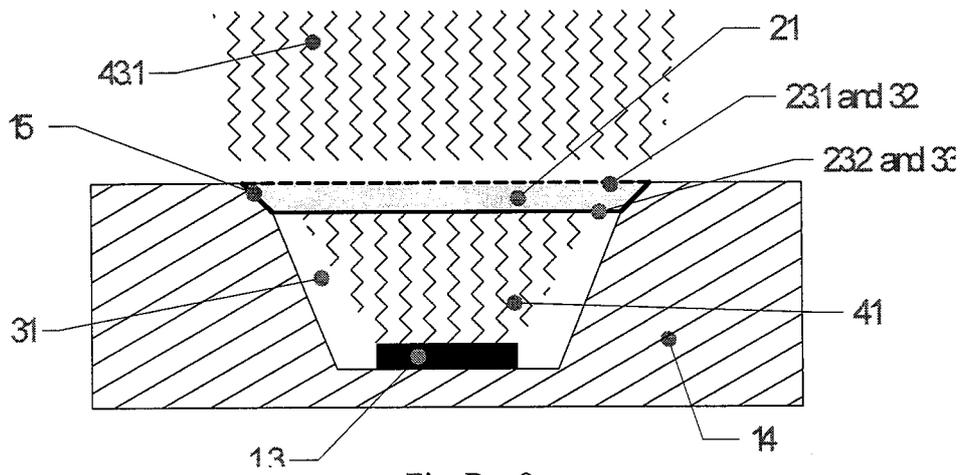


Fig. B - 8a

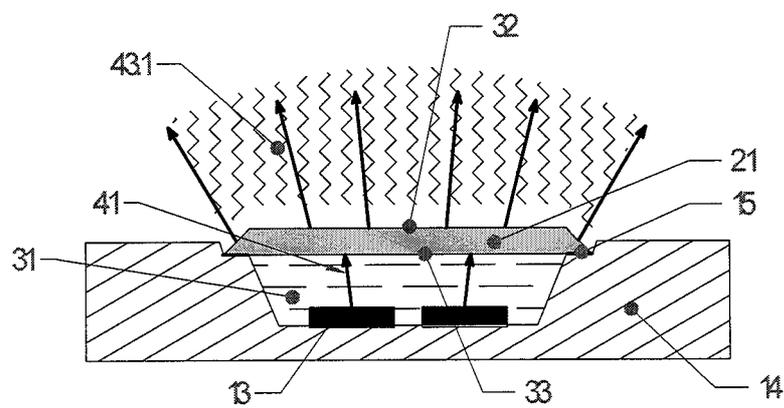


Fig. B - 8b

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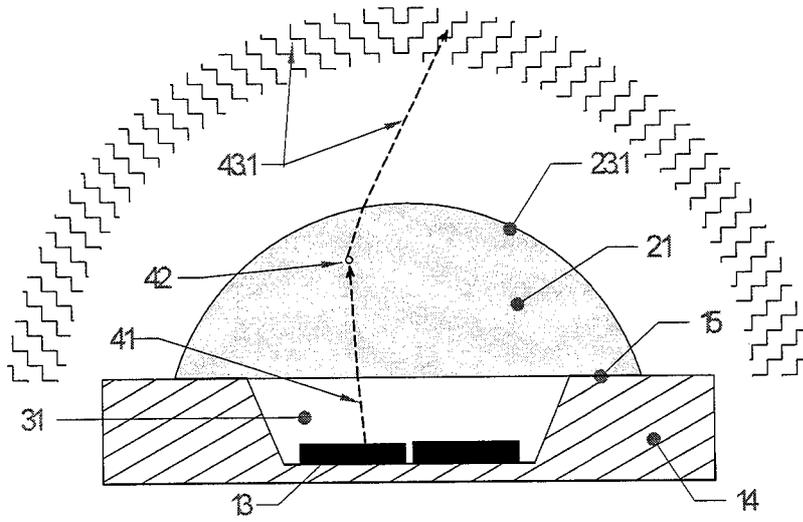


Fig. B - 9

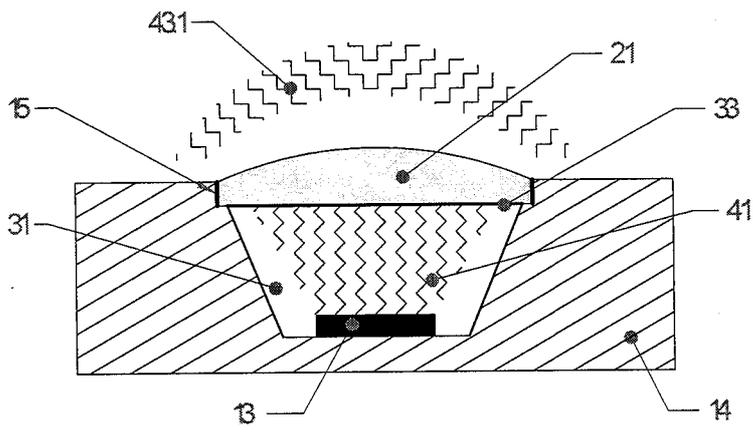


Fig. B - 10

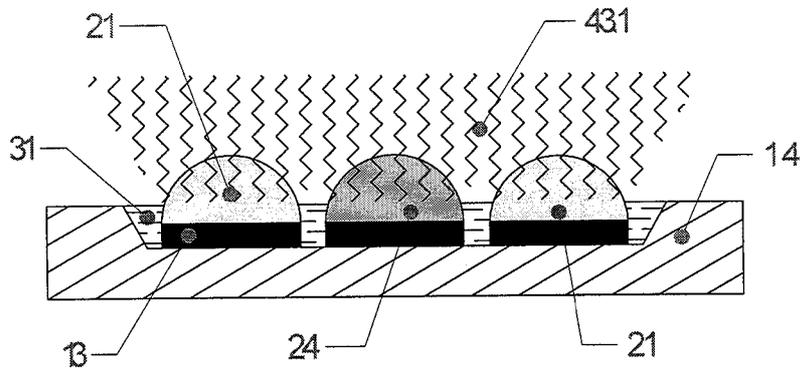


Fig. B - 12a

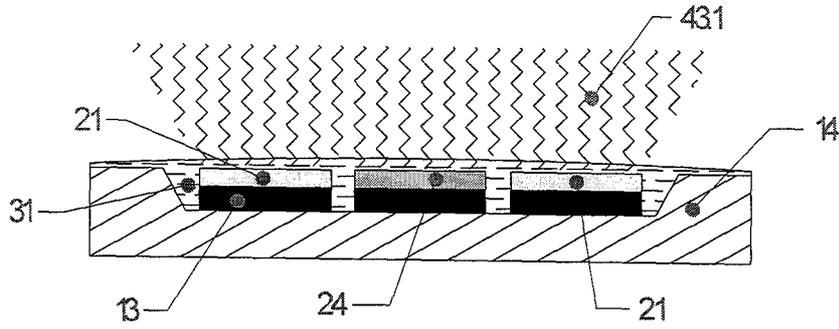


Fig. B - 12b

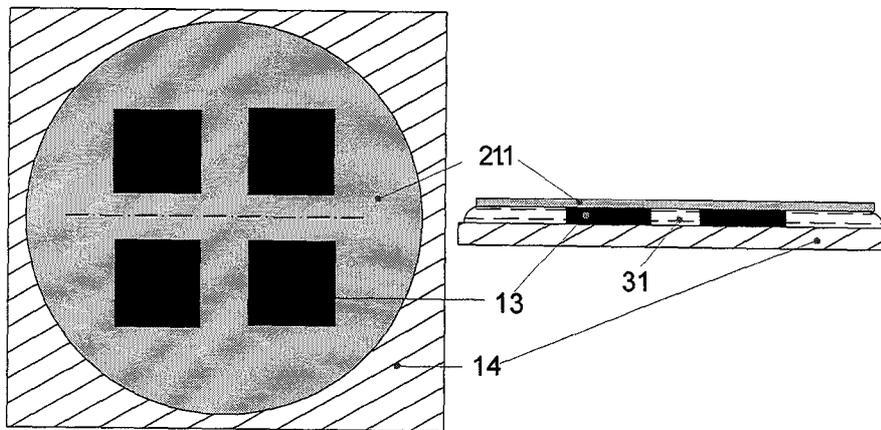


Fig. B - 13

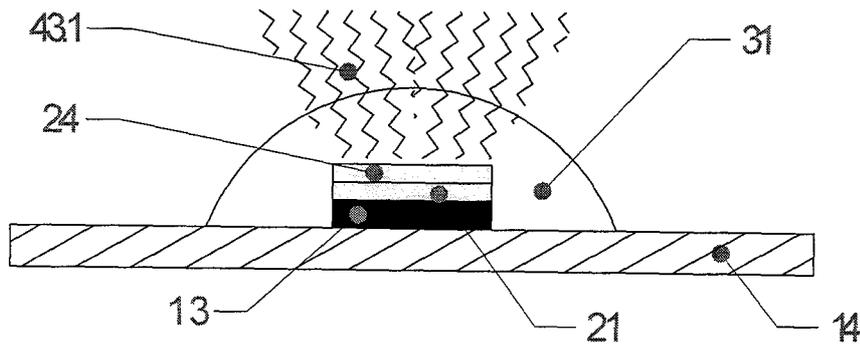


Fig. B - 14

INTERNATIONAL SEARCH REPORT

International application No PCT/CZ2014/000039

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K11/77
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 C30B B28D H01L

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	wo 2007/005013 AI (LAMINA CERAMICS INC [US]; BLONDER GREG [US]; AMAYA EDMAR [US]) 11 January 2007 (2007-01-11)	I - 6, 15-19
Y	page 6, lines 1-9; claims 1,6 page 5	7-9 , II- 14
X	-----	
X	DATABASE WPI Week 201314 Thomson Scientific, London, GB; AN 2013-C04016 XP002727658, - & CN 102 769 080 A (HANGZHOU SILAN AZURE CO LTD) 7 November 2012 (2012-11-07)	1-6
Y	abstract paragraph [0038]	7-9 , 11-14
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>
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Date of the actual completion of the international search 23 July 2014	Date of mailing of the international search report 31/07/2014
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Bal de, Kai sa
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INTERNATIONAL SEARCH REPORT

International application No

PCT/CZ2014/000039

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	EP 0 476 952 A2 (SHINETSU HANDOTAI KK [JP]) 25 March 1992 (1992-03-25) claims; examples -----	7-14
A	JP 2000 263499 A (SHINETSU CHEMICAL CO) 26 September 2000 (2000-09-26) abstract paragraphs [0021], [0022] -----	7-14
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Information on patent family members

International application No PCT/CZ2014/000039

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