

Description

LIGHT EMITTING DEVICE

Technical Field

- [1] The invention relates to light emitting devices and more particularly to light emitting devices including at least one light-emitting diode and phosphor, the phosphor including lead and/or copper doped chemical compounds and converting the wavelength of light.

Background Art

- [2] Light emitting devices (LEDs), which used to be used for electronic devices, are now used for automobiles and illumination products. Since light emitting devices have superior electrical and mechanical characteristics, demands for light emitting devices have been increased. In connection to this, interests in white LEDs are increasing as an alternative to fluorescent lamps and incandescent lamps.
- [3] In LED technology, solution for realization of white light is proposed variously. Normally, realization of white LED technology is to put the phosphor on the light-emitting diode, and mix the primary emission from the light emitting diode and the secondary emission from the phosphor, which converts the wavelength. For example, as shown in WO 98/05078 and WO 98/12757, use a blue light emitting diode, which is capable of emitting a peak wavelength at 450-490 nm, and YAG group material, which absorbs light from the blue light emitting diode and emits yellowish light (mostly), which may have different wavelength from that of the absorbed light
- [4] However, in such a usual white LED, color temperature range is narrow which is between about 6,000-8,000K, and CRI (Color Rendering Index) is about 60 to 75. Therefore, it is hard to produce the white LED with color coordination and color temperature that are similar to those of the visible light. It is one of the reasons why only white light color with a cold feeling could be realized. Moreover, phosphors which are used for white LEDs are usually unstable in the water, vapor or polar solvent, and this unstableness may cause changes in the emitting characteristics of white LED.

Disclosure of Invention

Technical Problem

- [5] Accordingly, the present invention is conceived to solve the aforementioned problems in the prior art. It is an object of the present invention to provide a light emitting device capable of providing wide range of color temperature from about 2,000K to about 8,000K or about 10,000K and/or color rendering index of greater than about 90.

- [6] Another object of the present invention is to provide a light emitting device in which desired color temperature or specific color coordination can be easily embodied.
- [7] An additional object of the present invention is to provide a light emitting device with improved luminescent properties and also with improved stability against water, humidity as well as other polar solvents.

Technical Solution

- [8] Wavelength conversion light emitting device are provided. In one embodiment consistent with this invention, a device is provided for emitting light. The device can include a substrate, a plurality of electrodes provided on the substrate, a light emitting diode configured to emit light, the light emitting diode being provided on one of the plurality of electrodes, phosphors configured to change a wavelength of the light, the phosphors substantially covering at least a portion of the light emitting diode, and an electrically conductive device configured to connect the light emitting diode with another of the plurality of electrodes.
- [9] In another embodiment consistent with this invention, a light emitting device can include a plurality of leads, a diode holder provided at the end of one of the plurality of lead, a light emitting diode provided in the diode holder, the light emitting diode including a plurality of electrodes, phosphors configured to change a wavelength of the light, the phosphors substantially covering at least a portion of the light emitting diode; and an electrically conductive device configured to connect the light emitting device with another of the plurality of leads.
- [10] In another embodiment consistent with this invention, a light emitting device may include a housing, a heat sink at least partially provided in the housing, a plurality of lead frames provided on the heat sink, a light emitting diode mounted on one of the plurality of lead frames, phosphors configured to change a wavelength of the light, the phosphors substantially covering at least a portion of the light emitting diode, and an electrically conductive device configured to connect the light emitting diode with another of the plurality of lead frames.
- [11] The phosphor in consistent with this invention may include aluminate type compounds, lead and/or copper doped silicates, lead and/or copper doped antimonates, lead and/or copper doped germanates, lead and/or copper doped germanate-silicates, lead and/or copper doped phosphates, or any combination thereof. Formulas for phosphors consistent with this invention are also provided.

Description of Drawings

- [12] Further aspects of the invention may be apparent upon consideration of the following detailed description, taken in conjunction with the accompanying drawings, in which like reference characters refer to like parts throughout, and in which:

- [13] Fig. 1 shows a side cross-sectional view of an illustrative embodiment of a portion of a chip-type package light emitting device consistent with this invention;
- [14] Fig. 2 shows a side cross-sectional view of an illustrative embodiment of a portion of a top-type package light emitting device consistent with this invention;
- [15] Fig. 3 shows a side cross-sectional view of an illustrative embodiment of a portion of a lamp-type package light emitting device consistent with this invention;
- [16] Fig. 4 shows a side cross-sectional view of an illustrative embodiment of a portion of a light emitting device for high power consistent with this invention;
- [17] Fig. 5 shows a side cross-sectional view of another illustrative embodiment of a portion of a light emitting device for high power consistent with this invention;
- [18] Fig. 6 shows emitting spectrum of a light emitting device with luminescent material consistent with this invention; and
- [19] Fig. 7 shows emitting spectrum of the light emitting device with luminescent material according to another embodiment of the invention.

Best Mode

- [20] Refer to the attached drawing, the wavelength conversion light emitting device is going to be explained in detail, and the light emitting device and the phosphor are separately explained for easiness of explanation as below.
- [21] (Light emitting device)
- [22] Fig. 1 shows a side cross-sectional view of an illustrative embodiment of a portion of a chip-type package light emitting device consistent with this invention. The chip-type package light emitting device may comprise at least one light emitting diode and a phosphorescent substance. Electrodes 5 may be formed on both sides of substrate 1. Light emitting diode 6 emitting light may be mounted on one of the electrodes 5. Light emitting diode 6 may be mounted on electrode 5 through electrically conductive paste 9. An electrode of light emitting diode 6 may be connected to electrode pattern 5 via an electrically conductive wire 2.
- [23] Light emitting diodes may emit light with a wide range of wavelengths, for example, from ultraviolet light to visible light. In one embodiment consistent with this invention, a UV light emitting diode and/or blue light emitting diode may be use.
- [24] Phosphor, i.e., a phosphorescent substance, 3 may be placed on the top and side faces of the light emitting diode 6. The phosphor in consistent with this invention may include lead and/or copper doped aluminate type compounds, lead and/or copper doped silicates, lead and/or copper doped antimonates, lead and/or copper doped germanates, lead and/or copper doped germanate-silicates, lead and/or copper doped phosphates, or any combination thereof. Phosphor 3 converts the wavelength of the light from the light emitting diode 6 to another wavelength or other wavelengths. In one embodiment consistent with this invention, the light is in a visible light range after the conversion. P

phosphor 3 may be applied to light emitting diode 6 after mixing phosphor 3 with a hardening resin. The hardening resin including phosphor 3 may also be applied to the bottom of light emitting diode 6 after mixing phosphor 3 with electrically conductive paste 9.

- [25] The light emitting diode 6 mounted on substrate 1 may be sealed with one or more sealing materials 10. Phosphor 3 may be placed on the top and side faces of light emitting diode 6. Phosphor 3 can also be distributed in the hardened sealing material during the production. Such a manufacturing method is described in U.S. Patent No. 6,482,664, which is hereby incorporated by reference in its entirety.
- [26] Phosphor 3 may comprise lead and/or copper doped chemical compound(s). Phosphor 3 may include one or more single chemical compounds. The single compound may have an emission peak of, for example, from about 440nm to about 500nm, from about 500nm to about 590nm, or from about 580nm to 700nm. Phosphor 3 may include one or more single phosphors, which may have an emission peak as exemplified above.
- [27] In regard to light emitting device 40, light emitting diode 6 may emit primary light when light emitting diode 6 receives power from a power supply. The primary light then may stimulate phosphor(s) 3, and phosphor(s) 3 may convert the primary light to a light with longer wavelength(s) (a secondary light). The primary light from the light emitting diode 6 and the secondary light from the phosphors 3 are diffused and mixed together so that a predetermined color of light in visible spectrum may be emitted from light emitting diode 6. In one embodiment consistent with this invention, more than one light emitting diodes that have different emission peaks can be mounted together. Moreover, if the mixture ratio of phosphors is adjusted properly, specific color of light, color temperature, and CRI can be provided.
- [28] As described above, if the light emitting diode 6 and the compound included in phosphor 3 are properly controlled then desired color temperature or specific color coordination can be provided, especially, wide range of color temperature, for example, from about 2,000K to about 8,000K or about 10,000K and/or color rendering index of greater than about 90. Therefore, the light emitting devices consistent with this invention may be used for electronic devices such as home appliances, stereos, telecommunication devices, and for interior/exterior custom displays. The light emitting devices consistent with this invention may also be used for automobiles and illumination products because they provide similar color temperatures and CRI to those of the visible light.
- [29] Fig. 2 shows a side cross-sectional view of an illustrative embodiment of a portion of a top-type package light emitting device consistent with this invention. A top-type package light emitting device consistent with this invention may have a similar

structure as that of the chip type package light emitting device 40 of Fig. 1. The top-type package device may have reflector 31 which may reflect the light from the light emitting diode 6 to the desire direction.

- [30] In top -type package light emitting device 50, more than one light emitting diodes can be mounted. Each of such light emitting diodes may have a different peak wavelength from that of others. Phosphor 3 may comprise a plurality of single compounds with different emission peak. The proportion of each of such plurality of compounds may be regulated. Such a phosphor may be applied to the light emitting diode and/or uniformly distributed in the hardening material of the reflector 31. As explained more fully below, the phosphor in consistent with this invention may include lead and/or copper doped aluminate type compounds, lead and/or copper doped silicates, lead and/or copper doped antimonates, lead and/or copper doped germanates, lead and/or copper doped germanate-silicates, lead and/or copper doped phosphates, or any combination thereof .
- [31] In one embodiment consistent with this invention, the light emitting device of the Fig. 1 or Fig. 2 can include a metal substrate, which may have good heat conductivity. Such a light emitting device may easily dissipate the heat from the light emitting diode. Therefore, light emitting devices for high power may be manufactured. If a heat sink is provided beneath the metal substrate, the heat from the light emitting diode may be dissipated more effectively.
- [32] Fig. 3 shows a side cross-sectional view of an illustrative embodiment of a portion of a lamp-type package light emitting device consistent with this invention. Lamp type light emitting device 60 may have a pair of leads 51, 52, and a diode holder 53 may be formed at the end of one lead. Diode holder 53 may have a shape of cup, and one or more light emitting diodes 6 may provided in the diode holder 53. When a number of light emitting diodes are provided in the diode holder 53, each of them may have a different peak wavelength from that of others. An electrode of light emitting diode 6 may be connected to lead 52 by, for example, electrically conductive wire 2.
- [33] Regular volume of phosphor 3, which may be mixed in the epoxy resin, may be provided in diode holder 53. As explained more fully below, phosphor 3 may include lead and/or copper doped components.
- [34] Moreover , the diode holder may include the light emitting diode 6 and the phosphor 3 may be sealed with hardening material such as epoxy resin or silicon resin.
- [35] In one embodiment consistent with this invention, the lamp type package light emitting device may have more than one pair of electrode pair leads.
- [36] Fig. 4 shows a side cross-sectional view of an illustrative embodiment of a portion of a light emitting device for high power consistent with this invention. Heat sink 71 may be provided inside of housing 73 of the light emitting device for high power 70,

and it may be partially exposed to outside. A pair of lead frame 74 may protrude from housing 73.

[37] One or more light emitting diodes may be mounted one lead frame 74, and an electrode of the light emitting diode 6 and another lead frame 74 may be connected via electrically conductive wire. Electrically conductive pate 9 may be provided between light emitting diode 6 and lead frame 74. The phosphor 3 may be placed on top and side faces of light emitting diode 6.

[38] Fig. 5 shows a side cross-sectional view of another illustrative embodiment of a portion of a light emitting device for high power consistent with this invention.

[39] Light emitting device for high power 80 may have housing 63, which may contain light emitting diodes 6, 7, phosphor 3 arranged on the top and side faces of light emitting diodes 6, 7, one or more heat sinks 61, 62, and one or more lead frames 64. The lead frames 64 may receive power from a power supplier and may protrude from housing 63.

[40] In the light emitting devices for high power 70, 80 in the Fig. 4 and 5, the phosphor 3 can be added to the paste, which may be provided between heat sink and light emitting devices. A lens may be combined with housing 63, 73.

[41] In a light emitting device for high power consistent with this invention, one or more light emitting diodes can be used selectively and the phosphor can be regulated depending on the light emitting diode. As explained more fully below, the phosphor may include lead and/or copper doped components.

[42] A light emitting device for high power consistent with this invention may have a radiator (not shown) and/or heat sink(s). Air or a fan may be used to cool the radiator.

[43] The light emitting devices consistent with this invention is not limited to the structures described above, and the structures can be modified depending on the characteristics of light emitting diodes, phosphor, wavelength of light, and also applications. Moreover, new part can be added to the structures.

[44] An exemplary phosphor consistent with this invention is as follows.

[45] (Phosphor)

[46] Phosphor in consistence with this invention may include lead and/or copper doped chemical compounds. The phosphor may be excited by UV and/or visible light, for example, blue light. The compound may include Aluminate, Silicate, Antimonate, Germanate, Germanate-silicate, or Phosphate type compounds.

[47] Aluminate type compounds may comprise compounds having formula (1), (2), and/or (5)

[48]
$$a(M'O) \cdot b(M''_2O) \cdot c(M''X) \cdot dAl_2O_3 \cdot e(M'''O) \cdot f(M''''_2O_3) \cdot g(M''''_oO_p) \cdot h(M''''''_xO_y) \dots (1)$$

[49] wherein M' may be Pb, Cu, and/or any combination thereof; M'' may be one or

more monovalent elements, for example, Li, Na, K, Rb, Cs, Au, Ag, and/or any combination thereof; M'' may be one or more divalent elements, for example, Be, Mg, Ca, Sr, Ba, Zn, Cd, Mn, and/or any combination thereof; M''' may be one or more trivalent elements, for example, Sc, B, Ga, In, and/or any combination thereof; M'''' may be Si, Ge, Ti, Zr, Mn, V, Nb, Ta, W, Mo, and/or any combination thereof; M''''' may be Bi, Sn, Sb, Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and/or any combination thereof; X may be F, Cl, Br, I, and/or any combination thereof; $0 < a \leq 2$; $0 \leq b \leq 2$; $0 \leq c \leq 2$; $0 \leq d \leq 8$; $0 < e \leq 4$; $0 \leq f \leq 3$; $0 \leq g \leq 8$; $0 < h \leq 2$; $1 \leq o \leq 2$; $1 \leq p \leq 5$; $1 \leq x \leq 2$; and $1 \leq y \leq 5$.

[50] $a(M'O) \cdot b(M''O) \cdot c(M''X) \cdot 4 - a - b$

[51] $-c(M'''O) \cdot 7(Al_2O_3) \cdot d(B_2O_3) \cdot e(Ga_2O_3) \cdot f(SiO_2) \cdot g(GeO_2) \cdot h(M''''O_x) \cdot \dots \dots (2)$

[52] wherein M' may be Pb, Cu, and/or any combination thereof; M'' may be one or more monovalent elements, for example, Li, Na, K, Rb, Cs, Au, Ag, and/or any combination thereof; M''' may be one or more divalent elements, for example, Be, Mg, Ca, Sr, Ba, Zn, Cd, Mn, and/or any combination thereof; M'''' may be Bi, Sn, Sb, Sc, Y, La, In, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and any combination thereof; X may be F, Cl, Br, I, and any combination thereof; $0 < a \leq 4$; $0 \leq b \leq 2$; $0 \leq c \leq 2$; $0 \leq d \leq 1$; $0 \leq e \leq 1$; $0 \leq f \leq 1$; $0 \leq g \leq 1$; $0 < h \leq 2$; $1 \leq x \leq 2$; and $1 \leq y \leq 5$.

[53] The preparation of copper as well as lead doped luminescent materials may be a basic solid state reaction. Pure starting materials without any impurities, e.g. iron, may be used. Any starting material which may transfer into oxides via a heating process may be used to form oxygen dominated phosphors.

[54] Examples of preparation:

[55] Preparation of the luminescent material having formula (3)

[56] $Cu_{0.02} Sr_{3.98} Al_{14} O_{25} : Eu \dots \dots (3)$

[57] Starting materials: CuO , $SrCO_3$, $Al(OH)_3$, Eu_2O_3 , and/or any combination thereof.

[58] The starting materials in the form of oxides, hydroxides, and/or carbonates may be mixed in stoichiometric proportions together with small amounts of flux, e.g., H_3BO_3 . The mixture may be fired in an alumina crucible in a first step at about 1,200 °C for about one hour. After milling the pre-fired materials a second firing step at about 1,450°C in a reduced atmosphere for about 4 hours may be followed. After that the material may be milled, washed, dried and sieved. The resulting luminescent material may have an emission maximum of about 494 nm.

[59] Table 1: copper doped Eu^{2+} -activated aluminate compared with Eu^{2+} -activated aluminate without copper at about 400 nm excitation wavelength

[60]

	Copper doped compound	Compound without copper
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	$\text{Cu}_{0.02} \text{Sr}_{3.98} \text{Al}_{14} \text{O}_{25} : \text{Eu}$	$\text{Sr}_4 \text{Al}_{14} \text{O}_{25} : \text{Eu}$
Luminous density (%)	103.1	100
Wavelength (nm)	494	493

[61] Preparation of the luminescent material having formula (4)

[62] $\text{Pb}_{0.05} \text{Sr}_{3.95} \text{Al}_{14} \text{O}_{25} : \text{Eu}$ (4)

[63] Starting materials: PbO , SrCO_3 , Al_2O_3 , Eu_2O_3 , and/or any combination thereof.

[64] The starting materials in form of very pure oxides, carbonates, or other components which may decompose thermally into oxides, may be mixed in stoichiometric proportion together with small amounts of flux, for example, H_3BO_3 . The mixture may be fired in an alumina crucible at about 1,200 °C for about one hour in the air. After milling the pre-fired materials a second firing step at about 1,450°C in air for about 2 hours and in a reduced atmosphere for about 2 hours may be followed. Then the material may be milled, washed, dried, and sieved. The resulting luminescent material may have an emission maximum of from about 494.5 nm.

[65] Table 2: lead doped Eu^{2+} -activated aluminate compared with Eu^{2+} -activated aluminate without lead at about 400 nm excitation wavelength

[66]

	Lead doped compound	Compound without lead
	$\text{Pb}_{0.05} \text{Sr}_{3.95} \text{Al}_{14} \text{O}_{25} : \text{Eu}$	$\text{Sr}_4 \text{Al}_{14} \text{O}_{25} : \text{Eu}$
Luminous density (%)	101.4	100
Wavelength (nm)	494.5	493

[67] Table 3: optical properties of some copper and/or lead doped aluminates excitable by long wave ultraviolet and/or by visible light and their luminous density in % at 400 nm excitation wavelength

[68]

Composition	Possible excitation range(nm)	Luminous density at 400 nm excitation compared with copper/lead not doped compounds (%)	Peak wave length of lead/copper doped materials (nm)	Peak wave length of materials without lead/copper (nm)
$\text{Cu}_{0.5} \text{Sr}_{3.5} \text{Al}_{14} \text{O}_{25} : \text{Eu}$	360 - 430	101.2	495	493

$\text{Cu}_{0.02} \text{Sr}_{3.98} \text{Al}_{14} \text{O}_{25} : \text{Eu}$	360 - 430	103.1	494	493
$\text{Pb}_{0.05} \text{Sr}_{3.95} \text{Al}_{14} \text{O}_{25} : \text{Eu}$	360 - 430	101.4	494.5	493
$\text{Cu}_{0.01} \text{Sr}_{3.99} \text{Al}_{13.99} \text{Si}_{0.005} \text{O}_{25} : \text{Eu}$	360 - 430	103	494	492
$\text{Cu}_{0.01} \text{Sr}_{3.395} \text{Ba}_{0.59} \text{Al}_{14} \text{O}_{25} : \text{Eu}, \text{Dy}$	360 - 430	100.8	494	493
$\text{Pb}_{0.05} \text{Sr}_{3.95} \text{Al}_{13.95} \text{Ga}_{0.05} \text{O}_{25} : \text{Eu}$	360 - 430	101.5	494	494

[69] $a(\text{M}'\text{O}) \cdot b(\text{M}''\text{O}) \cdot c(\text{Al}_2\text{O}_3) \cdot d(\text{M}'''\text{O}_3) \cdot e(\text{M}''''\text{O}_2) \cdot f(\text{M}'''''\text{O}_x) \cdot \text{O}_y \dots\dots (5)$

[70] wherein M' may be Pb, Cu, and/or any combination thereof; M'' may be Be, Mg, Ca, Sr, Ba, Zn, Cd, Mn, and/or any combination thereof; M''' may be B, Ga, In, and/or any combination thereof; M'''' may be Si, Ge, Ti, Zr, Hf, and/or any combination thereof; M''''' may be Bi, Sn, Sb, Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and/or any combination thereof; $0 < a \leq 1$; $0 \leq b \leq 2$; $0 < c \leq 8$; $0 \leq d \leq 1$; $0 \leq e \leq 1$; $0 < f \leq 2$; $1 \leq x \leq 2$; and $1 \leq y \leq 5$.

[71] Example of preparation:

[72] Preparation of the luminescent material having formula (6)

[73] $\text{Cu}_{0.05} \text{Sr}_{0.95} \text{Al}_{1.9997} \text{Si}_{0.0003} \text{O}_4 : \text{Eu} \dots\dots (6)$

[74] Starting materials: CuO , SrCO_3 , Al_2O_3 , SiO_2 , Eu_2O_3 , and/or any combination thereof.

[75] The starting materials in the form of, for example, pure oxides and/or as carbonates may be mixed in stoichiometric proportions together with small amounts of flux, for example, AlF_3 . The mixture may be fired in an alumina crucible at about 1,250°C in a reduced atmosphere for about 3 hours. After that the material may be milled, washed, dried and sieved. The resulting luminescent material may have an emission maximum of about 521.5 nm.

[76] Table 4: copper doped Eu^{2+} -activated aluminate compared with Eu^{2+} -activated aluminate without copper at about 400 nm excitation wavelength

[77]

	Copper doped compound	Compound without copper
	$\text{Cu}_{0.05} \text{Sr}_{0.95} \text{Al}_{1.9997} \text{Si}_{0.0003} \text{O}_4 : \text{Eu}$	$\text{SrAl}_2\text{O}_4 : \text{Eu}$

Luminous density (%)	106	100
Wavelength (nm)	521.5	519

[78] Preparation of the luminescent material having formula (7)

[79] $\text{Cu}_{0.12} \text{BaMg}_{1.88} \text{Al}_{16} \text{O}_{27} : \text{Eu}$ (7)

[80] Starting materials: CuO , MgO , BaCO_3 , Al(OH)_3 , Eu_2O_3 , and/or any combination thereof.

[81] The starting materials in the form of, for example, pure oxides, hydroxides, and/or carbonates may be mixed in stoichiometric proportions together with small amounts of flux, for example, AlF_3 . The mixture may be fired in an alumina crucible at about 1,420°C in a reduced atmosphere for about 2 hours. After that the material may be milled, washed, dried, and sieved. The resulting luminescent material may have an emission maximum of about 452 nm.

[82] Table 5: copper doped Eu^{2+} -activated aluminate compared with copper not doped Eu^{2+} -activated aluminate at 400 nm excitation wavelength

[83]

	Copper doped compound	Comparison without copper
	$\text{Cu}_{0.12} \text{BaMg}_{1.88} \text{Al}_{16} \text{O}_{27} : \text{Eu}$	$\text{BaMg}_2 \text{Al}_{16} \text{O}_{27} : \text{Eu}$
Luminous density (%)	101	100
Wavelength (nm)	452	450

[84] Preparation of the luminescent material having formula (8)

[85] $\text{Pb}_{0.1} \text{Sr}_{0.9} \text{Al}_2 \text{O}_4 : \text{Eu}$ (8)

[86] Starting materials: PbO , SrCO_3 , Al(OH)_3 , Eu_2O_3 , and/or any combination thereof.

[87] The starting materials in form of, for example, pure oxides, hydroxides, and/or carbonates may be mixed in stoichiometric proportions together with small amounts of flux, for example, H_3BO_3 . The mixture may be fired in an alumina crucible at about 1,000 °C for about 2 hours in the air. After milling the pre-fired materials a second firing step at about 1,420°C in the air for about 1 hour and in a reduced atmosphere for about 2 hours may be followed. After that the material may be milled, washed, dried and sieved. The resulting luminescent material may have an emission maximum of about 521 nm.

[88] Table 6: lead doped Eu^{2+} -activated aluminate compared with Eu^{2+} -activated aluminate without lead at about 400 nm excitation wavelength

[89]

	Lead doped compound	Compound without lead
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	$\text{Pb}_{0.1} \text{Sr}_{0.9} \text{Al}_2 \text{O}_4 : \text{Eu}$	$\text{SrAl}_2 \text{O}_4 : \text{Eu}$
Luminous density (%)	102	100
Wavelength (nm)	521	519

[90] Results obtained in regard to copper and/or lead doped aluminates are shown in table 7.

[91] Table 7: optical properties of some copper and/or lead doped aluminates excitable by long wave ultraviolet and/or by visible light and their luminous density in % at 400 nm excitation wavelength

[92]

Composition	Possible excitation range (nm)	Luminous density at 400 nm excitation compared with copper/lead not doped compounds (%)	Peak wave length of lead/copper doped materials (nm)	Peak wave length of materials without lead/copper (nm)
$\text{Cu}_{0.05} \text{Sr}_{0.95} \text{Al}_{1.9997} \text{Si}_{0.0003} \text{O}_4 : \text{Eu}$	360 - 440	106	521.5	519
$\text{Cu}_{0.2} \text{Mg}_{0.7995} \text{Li}_{0.0005} \text{Al}_{1.9} \text{Ga}_{0.1} \text{O}_4 : \text{Eu, Dy}$	360 - 440	101.2	482	480
$\text{Pb}_{0.1} \text{Sr}_{0.9} \text{Al}_2 \text{O}_4 : \text{Eu}$	360 - 440	102	521	519
$\text{Cu}_{0.05} \text{BaMg}_{1.95} \text{Al}_{16} \text{O}_{27} : \text{Eu, Mn}$	360 - 400	100.5	451, 515	450, 515
$\text{Cu}_{0.12} \text{BaMg}_{1.88} \text{Al}_{16} \text{O}_{27} : \text{Eu}$	360 - 400	101	452	450
$\text{Cu}_{0.01} \text{BaMg}_{0.99} \text{Al}_{10} \text{O}_{17} : \text{Eu}$	360 - 400	102.5	451	449
$\text{Pb}_{0.1} \text{BaMg}_{0.9} \text{Al}_{9.5} \text{Ga}_{0.5} \text{O}_{17} : \text{Eu, Dy}$	360 - 400	100.8	448	450
$\text{Pb}_{0.08} \text{Sr}_{0.902} \text{Al}_2 \text{O}_4 : \text{Eu, Dy}$	360 - 440	102.4	521	519
$\text{Pb}_{0.2} \text{Sr}_{0.8} \text{Al}_2 \text{O}_4 : \text{Mn}$	360 - 440	100.8	658	655
$\text{Cu}_{0.06} \text{Sr}_{0.94} \text{Al}_2 \text{O}_4 : \text{Eu}$	360 - 440	102.3	521	519
$\text{Cu}_{0.05} \text{Ba}_{0.94} \text{Pb}_{0.06} \text{Mg}_{0.95} \text{O}_4$	360 - 440	100.4	451	449

$\text{Al}_{10} \text{O}_{17} : \text{Eu}$				
$\text{Pb}_{0.3} \text{Ba}_{0.7} \text{Cu}_{0.1} \text{Mg}_{1.9} \text{Al}_{16} \text{O}_{27} : \text{Eu}$	360 - 400	100.8	452	450
$\text{Pb}_{0.3} \text{Ba}_{0.7} \text{Cu}_{0.1} \text{Mg}_{1.9} \text{Al}_{16} \text{O}_{27} : \text{Eu, Mn}$	360 - 400	100.4	452, 515	450, 515

[93] A lead and/or copper doped silicates having formula (9)

[94] $a(\text{M}'\text{O}) \cdot b(\text{M}''\text{O}) \cdot c(\text{M}'''\text{X}) \cdot d(\text{M}'''\text{O})_2 \cdot e(\text{M}''''\text{O})_2 \cdot f(\text{M}'''''\text{O})_p \cdot g(\text{SiO}_2) \cdot h(\text{M}''''''\text{O})_x \cdot y$
..... (9)

[95] wherein M' may be Pb, Cu, and/or any combination thereof; M'' may be Be, Mg, Ca, Sr, Ba, Zn, Cd, Mn, and/or any combination thereof; M''' may be Li, Na, K, Rb, Cs, Au, Ag, and/or any combination thereof; M'''' may be Al, Ga, In, and/or any combination thereof; M''''' may be Ge, V, Nb, Ta, W, Mo, Ti, Zr, Hf, and/or any combination thereof; M'''''' may be Bi, Sn, Sb, Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and/or any combination thereof; X may be F, Cl, Br, J, and any combination thereof; $0 < a \leq 2$; $0 < b \leq 8$; $0 \leq c \leq 4$; $0 \leq d \leq 2$; $0 \leq e \leq 2$; $0 \leq f \leq 2$; $0 \leq g \leq 10$; $0 < h \leq 5$; $1 \leq o \leq 2$; $1 \leq p \leq 5$; $1 \leq x \leq 2$; and $1 \leq y \leq 5$.

[96] Example of preparation:

[97] Preparation of the luminescent material having formula (10)

[98] $\text{Cu}_{0.05} \text{Sr}_{1.7} \text{Ca}_{0.25} \text{SiO}_4 : \text{Eu}$ (10)

[99] Starting materials: CuO , SrCO_3 , CaCO_3 , SiO_2 , Eu_2O_3 , and/or any combination thereof.

[100] The starting materials in the form of pure oxides and/or carbonates may be mixed in stoichiometric proportions together with small amounts of flux, for example, NH_4Cl . The mixture may be fired in an alumina crucible at about 1,200°C in an inert gas atmosphere (e.g., N_2 or noble gas) for about 2 hours. Then the material may be milled. After that, the material may be fired in an alumina crucible at about 1,200°C in a slightly reduced atmosphere for about 2 hours. Then, the material may be milled, washed, dried, and sieved. The resulting luminescent material may have an emission maximum at about 592 nm.

[101] Table 8: copper doped Eu^{2+} -activated silicate compared with Eu^{2+} -activated silicate without copper at about 400 nm excitation wavelength

[102]

	Copper doped compound	Compound without copper
	$\text{Cu}_{0.05} \text{Sr}_{1.7} \text{Ca}_{0.25} \text{SiO}_4 : \text{Eu}$	$\text{Sr}_{1.7} \text{Ca}_{0.3} \text{SiO}_4 : \text{Eu}$
Luminous density (%)	104	100
Wavelength (nm)	592	588

[103] Preparation of the luminescent material having formula (11):

[104] $\text{Cu}_{0.2} \text{Ba}_2 \text{Zn}_{0.2} \text{Mg}_{0.6} \text{Si}_2 \text{O}_7 : \text{Eu} \dots\dots (11)$

[105] Starting materials: CuO , BaCO_3 , ZnO , MgO , SiO_2 , Eu_2O_3 , and/or any combination thereof.

[106] The starting materials in the form of very pure oxides and carbonates may be mixed in stoichiometric proportions together with small amounts of flux, for example, NH_4Cl . In a first step the mixture may be fired in an alumina crucible at about $1,100^\circ\text{C}$ in a reduced atmosphere for about 2 hours. Then the material may be milled. After that the material may be fired in an alumina crucible at about $1,235^\circ\text{C}$ in a reduced atmosphere for about 2 hours. Then that the material may be milled, washed, dried and sieved. The resulting luminescent material may have an emission maximum at about 467 nm.

[107] Table 9: copper doped Eu^{2+} -activated silicate compared with Eu^{2+} -activated silicate without copper at 400 nm excitation wavelength

[108]

	Copper doped compound	Compound without copper
	$\text{Cu}_{0.2} \text{Sr}_2 \text{Zn}_{0.2} \text{Mg}_{0.6} \text{Si}_2 \text{O}_7 : \text{Eu}$	$\text{Sr}_2 \text{Zn}_2 \text{Mg}_{0.6} \text{Si}_2 \text{O}_7 : \text{Eu}$
Luminous density (%)	101.5	100
Wavelength (nm)	467	465

[109] Preparation of the luminescent material having formula (12)

[110] $\text{Pb}_{0.1} \text{Ba}_{0.95} \text{Sr}_{0.95} \text{Si}_{0.998} \text{Ge}_{0.002} \text{O}_4 : \text{Eu} \dots\dots (12)$

[111] Starting materials: PbO , SrCO_3 , BaCO_3 , SiO_2 , GeO_2 , Eu_2O_3 , and/or any combination thereof

[112] The starting materials in the form of oxides and/or carbonates may be mixed in stoichiometric proportions together with small amounts of flux, for example, NH_4Cl . The mixture may be fired in an alumina crucible at about $1,000^\circ\text{C}$ for about 2 hours in the air. After milling the pre-fired materials a second firing step at $1,220^\circ\text{C}$ in air for 4 hours and in reducing atmosphere for 2 hours may be followed. After that the material may be milled, washed, dried and sieved. The resulting luminescent material may have an emission maximum at about 527 nm.

[113] Table 10: lead doped Eu^{2+} -activated silicate compared with Eu^{2+} -activated silicate without lead at about 400 nm excitation wavelength

[114]

	Lead doped compound	Compound without lead
	$\text{Pb}_{0.1} \text{Ba}_{0.95} \text{Sr}_{0.95} \text{Si}_{0.998} \text{Ge}_{0.002}$	$\text{BaSrSiO}_4 : \text{Eu}$

	$O_4 : Eu$	
Luminous density (%)	101.3	100
Wavelength (nm)	527	525

[115] Preparation of the luminescent material having formula (13)

[116] $Pb_{0.25} Sr_{3.75} Si_3 O_8 Cl_4 : Eu$ (13)

[117] Starting materials : PbO , $SrCO_3$, $SrCl_2$, SiO_2 , Eu_2O_3 , and any combination thereof.

[118] The starting materials in the form of oxides, chlorides, and/or carbonates may be mixed in stoichiometric proportions together with small amounts of flux, for example, NH_4Cl . The mixture may be fired in an alumina crucible in a first step at about 1,100 °C for about 2 hours in the air. After milling the pre-fired materials a second firing step at about 1,220°C in the air for about 4 hours and in a reduced atmosphere for about 1 hour may be followed. After that the material may be milled, washed, dried and sieved. The resulting luminescent material may have an emission maximum at about 492 nm.

[119] Table 11: lead doped Eu^{2+} -activated chlorosilicate compared with Eu^{2+} -activated chlorosilicate without lead at 400 nm excitation wavelength

[120]

	Lead doped compound	Compound without lead
	$Pb_{0.25} Sr_{3.75} Si_3 O_8 Cl_4 : Eu$	$Sr_4 Si_3 O_8 Cl_4 : Eu$
Luminous density (%)	100.6	100
Wavelength (nm)	492	490

[121] Results obtained with respect to copper and/or lead doped silicates are shown in table 12.

[122] Table 12: optical properties of some copper and/or lead doped rare earth activated silicates excitable by long wave ultraviolet and/or by visible light and their luminous density in % at about 400 nm excitation wavelength:

[123]

Composition	Possible excitation range (nm)	Luminous density at 400nm excitation compared with copper/lead not doped compounds (%)	Peak wave length of lead/copper doped materials (nm)	Peak wave length of materials without lead/copper (nm)
$Pb_{0.1} Ba_{0.95} Sr_{0.95} Si$	360 - 470	101.3	527	525

$\text{Ge}_{0.998} \text{O}_{0.002} : \text{Eu}_4$				
$\text{Cu}_{0.02} (\text{Ba}, \text{Sr}, \text{Ca}, \text{Zn}) \text{SiO}_{1.98} : \text{Eu}_4$	360 - 500	108.2	565	560
$\text{Cu}_{0.05} \text{Sr}_{1.7} \text{Ca}_{0.25} \text{SiO}_4 : \text{Eu}_4$	360 - 470	104	592	588
$\text{Cu}_{0.05} \text{Li}_{0.002} \text{Sr}_{1.5} \text{Ba}_{0.448} \text{SiO}_4 : \text{Gd, Eu}_4$	360 - 470	102.5	557	555
$\text{Cu}_{0.2} \text{Sr}_2 \text{Zn}_2 \text{Mg}_{0.6} \text{Si}_2 \text{O}_7 : \text{Eu}_7$	360 - 450	101.5	467	465
$\text{Cu}_{0.02} \text{Ba}_{2.8} \text{Sr}_{0.2} \text{Mg}_{0.98} \text{SiO}_2 : \text{Eu, Mn}_8$	360 - 420	100.8	440, 660	438, 660
$\text{Pb}_{0.25} \text{Sr}_{3.75} \text{Si}_3 \text{O}_8 \text{Cl}_4 : \text{Eu}_4$	360 - 470	100.6	492	490
$\text{Cu}_{0.2} \text{Ba}_{2.2} \text{Sr}_{0.75} \text{Pb}_{0.05} \text{Zn}_{0.8} \text{SiO}_2 : \text{Eu}_8$	360 - 430	100.8	448	445
$\text{Cu}_{0.2} \text{Ba}_3 \text{Mg}_{0.8} \text{Si}_{1.99} \text{Ge}_{0.01} \text{O}_8 : \text{Eu}_8$	360 - 430	101	444	440
$\text{Cu}_{0.5} \text{Zn}_{0.5} \text{Ba}_2 \text{Ge}_{0.2} \text{Si}_{1.8} \text{O}_7 : \text{Eu}_7$	360 - 420	102.5	435	433
$\text{Cu}_{0.8} \text{Mg}_{0.2} \text{Ba}_3 \text{Si}_2 \text{O}_8 : \text{Eu, Mn}_8$	360 - 430	103	438, 670	435, 670
$\text{Pb}_{0.15} \text{Ba}_{1.84} \text{Zn}_{0.01} \text{Si}_{0.99} \text{Zr}_{0.01} \text{O}_4 : \text{Eu}_4$	360 - 500	101	512	510
$\text{Cu}_{0.2} \text{Ba}_5 \text{Ca}_{2.8} \text{Si}_4 \text{O}_{16} : \text{Eu}_{16}$	360 - 470	101.8	495	491

[124] With lead and/or copper doped antimonates having formula (14)

[125] $a(\text{M}'\text{O}) \cdot b(\text{M}''\text{O}) \cdot c(\text{M}'''\text{X}) \cdot d(\text{Sb}_2\text{O}_5) \cdot e(\text{M}'''\text{O}) \cdot f(\text{M}''''\text{O}_x)_y \dots\dots (14)$

[126] wherein M' may be Pb, Cu, and/or any combination thereof; M'' may be Li, Na, K, Rb, Cs, Au, Ag, and/or any combination thereof; M''' may be Be, Mg, Ca, Sr, Ba, Zn, Cd, Mn, and/or any combination thereof; M'''' may be Bi, Sn, Sc, Y, La, Pr, Sm, Eu, Tb, Dy, Gd, and/or any combination thereof; X may be F, Cl, Br, I, and/or any combination thereof; $0 < a \leq 2$; $0 \leq b \leq 2$; $0 \leq c \leq 4$; $0 < d \leq 8$; $0 \leq e \leq 8$; $0 \leq f \leq 2$; $1 \leq x \leq 2$; and $1 \leq y \leq 5$.

[127] Examples of preparation:

[128] Preparation of the luminescent material having formula (15)

[129] $\text{Cu}_{0.2} \text{Mg}_{1.7} \text{Li}_{0.2} \text{Sb}_2 \text{O}_7 : \text{Mn} \dots\dots (15)$

[130] Starting materials: CuO , MgO , $\text{Li}_2 \text{O}$, $\text{Sb}_2 \text{O}_5$, MnCO_3 , and/or any combination thereof.

[131] The starting materials in the form of oxides may be mixed in stoichiometric proportion together with small amounts of flux. In a first step the mixture may be fired in an alumina crucible at about 985°C in the air for about 2 hours. After pre-firing the material may be milled again. In a second step the mixture may be fired in an alumina crucible at about 1,200°C in an atmosphere containing oxygen for about 8 hours. After that the material may be milled, washed, dried and sieved. The resulting luminescent material may have an emission maximum at about 626 nm.

[132] Table 13: copper doped antimonate compared with antimonate without copper at about 400 nm excitation wavelength

[133]

	Copper doped compound	Comparison without copper
	$\text{Cu}_{0.2} \text{Mg}_{1.7} \text{Li}_{0.2} \text{Sb}_2 \text{O}_7 : \text{Mn}$	$\text{Mg}_{1.7} \text{Li}_{0.2} \text{Sb}_2 \text{O}_7 : \text{Mn}$
Luminous density (%)	101.8	100
Wavelength (nm)	652	650

[134] Preparation of the luminescent material having formula (16)

[135] $\text{Pb}_{0.006} \text{Ca}_{0.6} \text{Sr}_{0.394} \text{Sb}_2 \text{O}_6 \dots\dots (16)$

[136] Starting materials: PbO , CaCO_3 , SrCO_3 , $\text{Sb}_2 \text{O}_5$, and/or any combination thereof.

[137] The starting materials in the form of oxides and/or carbonates may be mixed in stoichiometric proportions together with small amounts of flux. In a first step the mixture may be fired in an alumina crucible at about 975°C in the air for about 2 hours. After pre-firing the material may be milled again. In a second step the mixture may be fired in an alumina crucible at about 1,175°C in the air for about 4 hours and then in an oxygen-containing atmosphere for about 4 hours. After that the material may be milled, washed, dried and sieved. The resulting luminescent material may have an emission maximum at about 637 nm.

[138] Table 14: lead doped antimonate compared with antimonate without lead at 400 nm excitation wavelength

[139]

	Lead doped compound	Compound without lead
	$\text{Pb}_{0.006} \text{Ca}_{0.6} \text{Sr}_{0.394} \text{Sb}_2 \text{O}_6$	$\text{Ca}_{0.6} \text{Sr}_{0.4} \text{Sb}_2 \text{O}_6$

Luminous density (%)	102	100
Wavelength (nm)	637	638

[140] Results obtained in respect to copper and/or lead doped antimonates are shown in table 15.

[141] Table 15: optical properties of some copper and/or lead doped antimonates excitable by long wave ultraviolet and/or by visible light and their luminous density in % at about 400 nm excitation wavelength

[142]

Composition	Possible excitation range (nm)	Luminous density at 400 nm excitation compared with copper/lead not doped compounds (%)	Peak wave length of lead/copper doped materials (nm)	Peak wave length of materials without lead/copper (nm)
$\text{Pb}_{0.2} \text{Mg}_{0.002} \text{Ca}_{1.798} \text{Sb}_2 \text{O}_6 \text{F}_2 : \text{Mn}$	360 - 400	102	645	649
$\text{Cu}_{0.15} \text{Ca}_{1.845} \text{Sr}_{0.005} \text{Sb}_2 \text{O}_7 : \text{Mn}$	360 - 400	101.5	660	658
$\text{Cu}_{0.2} \text{Mg}_{1.7} \text{Li}_{0.2} \text{Sb}_2 \text{O}_7 : \text{Mn}$	360 - 400	101.8	652	650
$\text{Cu}_{0.2} \text{Pb}_{0.01} \text{Ca}_{0.79} \text{Sb}_{1.98} \text{Nb}_{0.02} \text{O}_6 : \text{Mn}$	360 - 400	98.5	658	658
$\text{Cu}_{0.01} \text{Ca}_{1.99} \text{Sb}_{1.9995} \text{V}_{0.0005} \text{O}_7 : \text{Mn}$	360 - 400	100.5	660	657
$\text{Pb}_{0.006} \text{Ca}_{0.6} \text{Sr}_{0.394} \text{Sb}_2 \text{O}_6$	360 - 400	102	637	638
$\text{Cu}_{0.02} \text{Ca}_{0.9} \text{Sr}_{0.5} \text{Ba}_{0.4} \text{Mg}_{0.18} \text{Sb}_2 \text{O}_7$	360 - 400	102.5	649	645
$\text{Pb}_{0.198} \text{Mg}_{0.004} \text{Ca}_{1.798} \text{Sb}_2 \text{O}_6 \text{F}_2$	360 - 400	101.8	628	630

[143] Lead and/or copper doped germanates and/or a germanate-silicates having formula (17)

[144] $a(\text{M}'\text{O}) \cdot b(\text{M}''\text{O}) \cdot c(\text{M}'''\text{X}) \cdot d\text{GeO}_2 \cdot e(\text{M}'''\text{O}) \cdot f(\text{M}''''\text{O}_3) \cdot g(\text{M}'''''\text{O}_p) \cdot h(\text{M}''''''\text{O}_x) \cdot \dots$

(17)

[145] wherein M' may be Pb, Cu, and/or any combination thereof; M'' may be Li, Na, K, Rb, Cs, Au, Ag, and/or any combination thereof; M''' may be Be, Mg, Ca, Sr, Ba, Zn, Cd, and/or any combination thereof; M'''' may be Sc, Y, B, Al, La, Ga, In, and/or any combination thereof; M''''' may be Si, Ti, Zr, Mn, V, Nb, Ta, W, Mo, and/or any combination thereof; M'''''' may be Bi, Sn, Pr, Sm, Eu, Gd, Dy, and/or any combination thereof; X may be F, Cl, Br, I, and/or any combination thereof; $0 < a \leq 2$; $0 \leq b \leq 2$; $0 \leq c \leq 10$; $0 < d \leq 10$; $0 \leq e \leq 14$; $0 \leq f \leq 14$; $0 \leq g \leq 10$; $0 \leq h \leq 2$; $1 \leq o \leq 2$; $1 \leq p \leq 5$; $1 \leq x \leq 2$; and $1 \leq y \leq 5$.

[146] Example of preparation:

[147] Preparation of the luminescent material having formula (18)

[148] $\text{Pb}_{0.004} \text{Ca}_{1.99} \text{Zn}_{0.006} \text{Ge}_{0.8} \text{Si}_{0.2} \text{O}_4 : \text{Mn} \dots\dots (18)$

[149] Starting materials: PbO , CaCO_3 , ZnO , GeO_2 , SiO_2 , MnCO_3 , and/or any combination thereof,

[150] The starting materials in the form of oxides and/or carbonates may be mixed in stoichiometric proportions together with small amounts of flux, for example, NH_4Cl . In a first step the mixture may be fired in an alumina crucible at about $1,200^\circ\text{C}$ in an oxygen-containing atmosphere for about 2 hours. Then, the material may be milled again. In a second step the mixture may be fired in an alumina crucible at about $1,200^\circ\text{C}$ in oxygen containing atmosphere for about 2 hours. After that the material may be milled, washed, dried and sieved. The resulting luminescent material may have an emission maximum at about 655 nm.

[151] Table 16: lead doped Mn-activated germanate compared with Mn-activated germanate without lead at about 400 nm excitation wavelength

[152]

	Copper doped compound	Comparison without copper
	$\text{Pb}_{0.004} \text{Ca}_{1.99} \text{Zn}_{0.006} \text{Ge}_{0.8} \text{Si}_{0.2} \text{O}_4 : \text{Mn}$	$\text{Ca}_{1.99} \text{Zn}_{0.01} \text{Ge}_{0.8} \text{Si}_{0.2} \text{O}_4 : \text{Mn}$
Luminous density (%)	101.5	100
Wavelength (nm)	655	657

[153] Preparation of the luminescent material having formula (19)

[154] $\text{Cu}_{0.46} \text{Sr}_{0.54} \text{Ge}_{0.6} \text{Si}_{0.4} \text{O}_3 : \text{Mn} \dots\dots (19)$

[155] Starting materials : CuO , SrCO_3 , GeO_2 , SiO_2 , MnCO_3 , and/or any combination thereof

[156] The starting materials in the form of oxides and/or carbonates may be mixed in sto-

ichiometric proportions together with small amounts of flux, for example, NH_4Cl . In a first step the mixture may be fired in an alumina crucible at about $1,100^\circ\text{C}$ in an oxygen-containing atmosphere for about 2 hours. Then, the material may be milled again. In a second step the mixture may be fired in an alumina crucible at about $1,180^\circ\text{C}$ in an oxygen-containing atmosphere for about 4 hours. After that the material may be milled, washed, dried and sieved. The resulting luminescent material may have an emission maximum at about 658 nm.

[157] Table 17: copper doped Mn-activated germanate-silicate compared with Mn-activated germanate-silicate without copper at 400 nm excitation wavelength

[158]

	Copper doped compound	Compound without copper
	$\text{Cu}_{0.46} \text{Sr}_{0.54} \text{Ge}_{0.6} \text{Si}_{0.4} \text{O}_3 : \text{Mn}$	$\text{SrGe}_{0.6} \text{Si}_{0.4} \text{O}_3 : \text{Mn}$
Luminous density (%)	103	100
Wavelength (nm)	658	655

[159] Table 18: optical properties of some copper and/or lead doped germanate-silicates excitable by long wave ultraviolet and/or by visible light and their luminous density in % at about 400 nm excitation wavelength

[160]

Composition	Possible excitation range (nm)	Luminous density at 400 nm excitation compared with copper/lead not doped compounds (%)	Peak wave length of lead/copper doped materials (nm)	Peak wave length of materials without lead/copper (nm)
$\text{Pb}_{0.004} \text{Ca}_{1.99} \text{Zn}_{0.006} \text{Ge}_{0.8} \text{Si}_{0.2} \text{O}_4 : \text{Mn}$	360 - 400	101.5	655	657
$\text{Pb}_{0.002} \text{Sr}_{0.954} \text{Ca}_{1.044} \text{Ge}_{0.93} \text{Si}_{0.07} \text{O}_4 : \text{Mn}$	360 - 400	101.5	660	661
$\text{Cu}_{0.46} \text{Sr}_{0.54} \text{Ge}_{0.6} \text{Si}_{0.4} \text{O}_3 : \text{Mn}$	360 - 400	103	658	655
$\text{Cu}_{0.002} \text{Sr}_{0.998} \text{Ba}_{0.99} \text{Ca}_{0.01} \text{Si}_{0.98} \text{Ge}_{0.02} \text{O}_4 : \text{Eu}$	360 - 470	102	538	533
$\text{Cu}_{1.45} \text{Mg}_{26.55} \text{Ge}_{9.4} \text{Si}_{0.6} \text{O}$	360 -	102	660	657

$\text{Cu}_{48} : \text{Mn}$	400			
$\text{Cu}_{1.2} \text{Mg}_{26.8} \text{Ge}_{8.9} \text{Si}_{1.1} \text{O}_{48} : \text{Mn}$	360 - 400	103.8	670	656
$\text{Cu}_4 \text{Mg}_{20} \text{Zn}_4 \text{Ge}_5 \text{Si}_{2.5} \text{O}_{38} \text{F}_{10} : \text{Mn}$	360 - 400	101.5	658	655
$\text{Pb}_{0.001} \text{Ba}_{0.849} \text{Zn}_{0.05} \text{Sr}_{1.1} \text{Ge}_{0.04} \text{Si}_{0.96} \text{O}_4 : \text{Eu}$	360 - 470	101.8	550	545
$\text{Cu}_{0.05} \text{Mg}_{4.95} \text{GeO}_6 \text{F}_2 : \text{Mn}$	360 - 400	100.5	655	653
$\text{Cu}_{0.05} \text{Mg}_{3.95} \text{GeO}_{5.5} \text{F} : \text{Mn}$	360 - 400	100.8	657	653

[161] Lead and/or copper doped phosphates having formula (20)

[162] $a(\text{M}'\text{O}) \cdot b(\text{M}''\text{O}) \cdot c(\text{M}'''\text{X}) \cdot d\text{P}_2\text{O}_5 \cdot e(\text{M}'''\text{O}) \cdot f(\text{M}''''\text{O}_2) \cdot g(\text{M}'''''\text{O}_2) \cdot h(\text{M}'''''\text{O}_x) \dots\dots$
(20)

[163] wherein M' may be Pb, Cu, and/or any combination thereof; M'' may be Li, Na, K, Rb, Cs, Au, Ag, and/or any combination thereof; M''' may be Be, Mg, Ca, Sr, Ba, Zn, Cd, Mn, and/or any combination thereof; M'''' may be Sc, Y, B, Al, La, Ga, In, and/or any combination thereof; M''''' may be Si, Ge, Ti, Zr, Hf, V, Nb, Ta, W, Mo, and/or any combination thereof; M'''''' may be Bi, Sn, Pr, Sm, Eu, Gd, Dy, Ce, Tb, and/or any combination thereof; X may be F, Cl, Br, J, and/or any combination thereof; $0 < a \leq 2$; $0 \leq b \leq 12$; $0 \leq c \leq 16$; $0 < d \leq 3$; $0 \leq e \leq 5$; $0 \leq f \leq 3$; $0 \leq g \leq 2$; $0 < h \leq 2$; $1 \leq x \leq 2$; and $1 \leq y \leq 5$.

[164] Examples of preparation:

[165] Preparation of the luminescent material having formula (21)

[166] $\text{Cu}_{0.02} \text{Ca}_{4.98} (\text{PO}_4)_3 \text{Cl} : \text{Eu} \dots\dots$ (21)

[167] Starting materials: CuO , CaCO_3 , $\text{Ca}_3(\text{PO}_4)_2$, CaCl_2 , Eu_2O_3 , and/or any combination thereof,

[168] The starting materials in the form of oxides, phosphates, and/or carbonates and chlorides may be mixed in stoichiometric proportions together with small amounts of flux. The mixture may be fired in an alumina crucible at about 1,240°C in reducing atmosphere for about 2 hours. After that the material may be milled, washed, dried and sieved. The luminescent material may have an emission maximum at about 450 nm.

[169] Table 19: copper doped Eu^{2+} -activated chlorophosphate compared with Eu^{2+} -activated chlorophosphate without copper at about 400 nm excitation wavelength

[170]

	Copper doped compound	Compound without copper
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	$\text{Cu}_{0.02} \text{Ca}_{4.98} (\text{PO})_4 \text{Cl} : \text{Eu}$	$\text{Ca}_5 (\text{PO})_4 \text{Cl} : \text{Eu}$
Luminous density (%)	101.5	100
Wavelength (nm)	450	447

[171] Table 20: copper and/or lead doped phosphates excitable by long wave ultraviolet and/or by visible light and their luminous density in % at about 400 nm excitation wavelength

[172]

Composition	Possible excitation range (nm)	Luminous density at 400 nm excitation compared with copper/lead not doped compounds (%)	Peak wave length of lead/copper doped materials (nm)	Peak wave length of materials without lead/copper (nm)
$\text{Cu}_{0.02} \text{Sr}_{4.98} (\text{PO})_4 \text{Cl} : \text{Eu}$	360 - 410	101.5	450	447
$\text{Cu}_{0.2} \text{Mg}_{0.8} \text{BaP}_2 \text{O}_7 : \text{Eu, Mn}$	360 - 400	102	638	635
$\text{Pb}_{0.5} \text{Sr}_{1.5} \text{P}_{1.84} \text{B}_{0.16} \text{O}_{6.84} : \text{Eu}$	360 - 400	102	425	420
$\text{Cu}_{0.5} \text{Mg}_{0.5} \text{Ba}_2 (\text{P,Si}) \text{O}_{28} : \text{Eu}$	360 - 400	101	573	570
$\text{Cu}_{0.5} \text{Sr}_{9.5} (\text{P,B})_6 \text{O}_{24} \text{Cl}_2 : \text{Eu}$	360 - 410	102	460	456
$\text{Cu}_{0.5} \text{Ba}_3 \text{Sr}_{6.5} \text{P}_6 \text{O}_{24} (\text{F,Cl})_2 : \text{Eu}$	360 - 410	102	443	442
$\text{Cu}_{0.05} (\text{Ca,Sr,Ba})_{4.95} \text{P}_3 \text{O}_{12} \text{Cl} : \text{Eu, Mn}$	360 - 410	101.5	438, 641	435, 640
$\text{Pb}_{0.1} \text{Ba}_{2.9} \text{P}_2 \text{O}_8 : \text{Eu}$	360 - 400	103	421	419

[173] Meanwhile, the phosphor of the light emitting device consistent with this invention can comprise aluminate, silicate, antimonate, germanate, phosphate type chemical compound, and any combination thereof.

[174] Fig. 6 is a one of the embodiment's emission spectrum according to the invention, which the phosphor is used for the light emitting device. The embodiment may have a

light emitting diode with 405nm wavelength and the phosphor, which is mixture of the selected multiple chemical compounds in proper ratio. The phosphor may be composed of $\text{Cu}_{0.05}\text{BaMg}_{1.95}\text{Al}_{16}\text{O}_{27} : \text{Eu}$ which may have peak wavelength at about 451nm, $\text{Cu}_{0.03}\text{Sr}_{1.5}\text{Ca}_{0.47}\text{SiO}_4 : \text{Eu}$ which may have peak wavelength at 586nm, $\text{Pb}_{0.006}\text{Ca}_{0.6}\text{Sr}_{0.394}\text{Sb}_2\text{O}_6$: Mn^{4+} which may have peak wavelength at about 637nm, $\text{Pb}_{0.15}\text{Ba}_{1.84}\text{Zn}_{0.01}\text{Si}_{0.99}\text{Zr}_{0.01}\text{O}_4$: Eu which may have peak wavelength at around 512nm, and $\text{Cu}_{0.2}\text{Sr}_{3.8}\text{Al}_{14}\text{O}_{25} : \text{Eu}$ which may have peak wavelength at about 494nm.

[175] In such an embodiment, part of the initial about 405nm wavelength emission light from the light emitting diode is absorbed by the phosphor, and it is converted to longer 2nd wavelength. The 1st and 2nd light is mixed together and the desire emission is produced. As the shown Fig. 6, the light emitting device convert the 1st UV light of 405nm wavelength to wide spectral range of visible light, that is, white light, and at this time the color temperature is about 3,000K and CRI is about 90 to about 95.

[176] Fig. 7 is another embodiment's emission spectrum according to the invention, which the phosphor is applied for the light emitting device. The embodiment may have a light emitting diode with about 455nm wavelength and the phosphor, which is mixture of the selected multiple chemical compounds in proper ratio.

[177] The phosphor is composed of $\text{Cu}_{0.05}\text{Sr}_{1.7}\text{Ca}_{0.25}\text{SiO}_4 : \text{Eu}$ which may have peak wavelength at about 592nm, $\text{Pb}_{0.1}\text{Ba}_{0.95}\text{Sr}_{0.95}\text{Si}_{0.998}\text{Ge}_{0.002}\text{O}_4$: Eu which may have peak wavelength at about 527nm, and $\text{Cu}_{0.05}\text{Li}_{0.002}\text{Sr}_{1.5}\text{Ba}_{0.448}\text{SiO}_4$: Gd , Eu which may have peak wavelength at about 557nm.

[178] In such an embodiment, part of the initial about 455nm wavelength emission light from the light emitting diode is absorbed by the phosphor, and it is converted to longer 2nd wavelength. The 1st and 2nd light is mixed together and the desire emission is produced. As the shown Fig. 7, the light emitting device convert the 1st blue light of about 455nm wavelength to wide spectral range of visible light, that is, white light, and at this time the color temperature is about 4,000K to about 6,500K and CRI is about 86 to about 93.

[179] The phosphor of the light emitting device according to the invention can be applied by single chemical compound or mixture of plurality of single chemical compound besides the embodiments in relation to Fig. 6 and Fig. 7, which are explained above.

[180] According to the description above, light emitting device with wide range of color temperature about 2,000K or about 8,000K or about 10,000K and superior color rendering index more than about 90 can be realized by using the lead and/or copper doped chemical compounds containing rare earth elements.

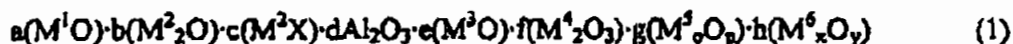
Industrial Applicability

[181] In such a wavelength conversion light emitting device is capable of applying on mobile phone, note book and electronic devices such as home appliance, stereo,

telecommunication products, but also for custom display's key pad and back light application. Moreover, it can be applied for automobile, medical instrument and illumination products.

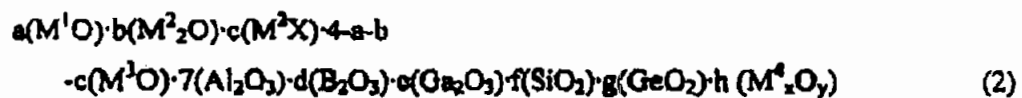
[182] According to the invention, it is also able to provide a wavelength conversion light emitting device with stability against water, humidity, vapor as well as other polar solvents.

[183] In the foregoing described embodiments, various features are grouped together in a single embodiment for purposes of streamlining the disclosure. This method of disclosure is not to be interpreted as reflecting an intention that the claimed invention requires more features than are expressly recited in each claim. Rather, as the following claims reflect, inventive aspects lie in less than all features of a single foregoing disclosed embodiment. Thus, the following claims are hereby incorporated into this Detailed Description of Embodiments, with each claim standing on its own as a separate preferred embodiment of the invention.

WHAT IS CLAIMED IS:**1. A light emitting device, comprising:****a substrate;****a plurality of electrodes provided on the substrate;****a light emitting diode configured to emit light, the light emitting diode being provided on one of the plurality of electrodes;****a phosphor configured to change a wavelength of the light, the phosphor substantially covering at least a portion of the light emitting diode; and****an electrically conductive device configured to connect the light emitting diode with another of the plurality of electrodes,****wherein the phosphor comprises an aluminate containing lead and/or copper, a silicate containing lead and/or copper, an antimonate containing lead and/or copper, a germanate containing lead and/or copper, a germanate-silicate containing lead and/or copper, a phosphate containing lead and/or copper, or any combination thereof.****2. The light emitting device according to claim 1, wherein the phosphor includes a compound having formula (1)****wherein****M¹ is Pb, Cu, or any combination thereof;****M² is Li, Na, K, Rb, Cs, Au, Ag or any combination thereof;****M³ is Be, Mg, Ca, Sr, Ba, Zn, Cd, Mn or any combination thereof;****M⁴ is Sc, B, Ga, In, or any combination thereof;****M⁵ is Si, Ge, Ti, Zr, Mn, V, Nb, Ta, W, Mo, or any combination thereof;****M⁶ is Bi, Sn, Sb, Se, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, or any combination thereof;****X is F, Cl, Br, I, or any combination thereof;****0 < a ≤ 2;****0 ≤ b ≤ 2;**

$$\begin{aligned}
0 &\leq c \leq 2; \\
0 &\leq d \leq 8; \\
0 &< e \leq 4; \\
0 &\leq f \leq 3; \\
0 &\leq g \leq 8; \\
0 &< h \leq 2; \\
1 &\leq o \leq 3; \\
1 &\leq p \leq 5; \\
1 &\leq x \leq 2; \text{ and} \\
1 &\leq y \leq 5.
\end{aligned}$$

3. The light emitting device according to claim 1, wherein the phosphor includes a compound having formula (2)



wherein

M^1 is Pb, Cu, or any combination thereof;

M^2 is Li, Na, K, Rb, Cs, Au, Ag, or any combination thereof;

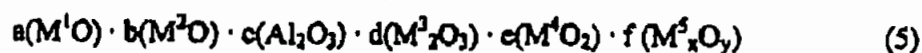
M^3 is Be, Mg, Ca, Sr, Ba, Zn, Cd, Mn, or any combination thereof;

M^4 is Bi, Sn, Sb, Sc, Y, La, In, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, or any combination thereof;

X is F, Cl, Br, I, or any combination thereof;

$$\begin{aligned}
0 &< a \leq 4; \\
0 &\leq b \leq 2; \\
0 &\leq c \leq 2; \\
0 &\leq d \leq 1; \\
0 &\leq e \leq 1; \\
0 &\leq f \leq 1; \\
0 &\leq g \leq 1; \\
0 &< h \leq 2; \\
1 &\leq x \leq 2; \text{ and} \\
1 &\leq y \leq 5.
\end{aligned}$$

4. The light emitting device according to claim 1, wherein the phosphor includes a compound having formula (5)



wherein

M^1 is Pb, Cu, or any combination thereof;

M^2 is Be, Mg, Ca, Sr, Ba, Zn, Cd, Mn, or any combination thereof;

M^3 is B, Ga, In, or any combination thereof;

M^4 is Si, Ge, Ti, Zr, Hf, or any combination thereof;

M^5 is Bi, Sn, Sb, Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, or any combination thereof;

$$0 < a \leq 1;$$

$$0 \leq b \leq 2;$$

$$0 < c \leq 8;$$

$$0 \leq d \leq 1;$$

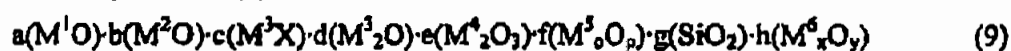
$$0 \leq e \leq 1;$$

$$0 < f \leq 2;$$

$$1 \leq x \leq 2; \text{ and}$$

$$1 \leq y \leq 5.$$

5. The light emitting device according to claim 1, wherein the phosphor includes a compound having formula (9)



wherein

M^1 is Pb, Cu, or any combination thereof;

M^2 is Be, Mg, Ca, Sr, Ba, Zn, Cd, Mn, or any combination thereof;

M^3 is Li, Na, K, Rb, Cs, Au, Ag, or any combination thereof;

M^4 is Al, Ga, In, or any combination thereof;

M^5 is Ge, V, Nb, Ta, W, Mo, Ti, Zr, Hf, or any combination thereof;

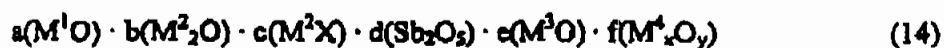
M^6 is Bi, Sn, Sb, Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, or any combination thereof;

X is F, Cl, Br, I, or any combination thereof;

$$0 < a \leq 2;$$

$$\begin{aligned}
0 < b &\leq 8; \\
0 \leq c &\leq 4; \\
0 \leq d &\leq 2; \\
0 \leq e &\leq 2; \\
0 \leq f &\leq 2; \\
0 \leq g &\leq 10; \\
0 < h &\leq 5; \\
1 \leq o &\leq 2; \\
1 \leq p &\leq 5; \\
1 \leq x &\leq 2; \text{ and} \\
1 \leq y &\leq 5.
\end{aligned}$$

6. The light emitting device according to claim 1, wherein the phosphor includes a compound having formula (14)



wherein

M^1 is Pb, Cu, or any combination thereof;

M^2 is Li, Na, K, Rb, Cs, Au, Ag, or any combination thereof;

M^3 is Be, Mg, Ca, Sr, Ba, Zn, Cd, Mn, or any combination thereof;

M^4 is Bi, Sn, Sc, Y, La, Pr, Sm, Eu, Tb, Dy, Gd, or any combination thereof;

X is F, Cl, Br, I, or any combination thereof;

$$0 < a \leq 2;$$

$$0 \leq b \leq 2;$$

$$0 \leq c \leq 4;$$

$$0 < d \leq 8;$$

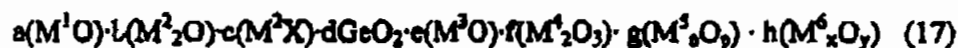
$$0 \leq e \leq 8;$$

$$0 \leq f \leq 2;$$

$$1 \leq x \leq 2; \text{ and}$$

$$1 \leq y \leq 5.$$

7. The light emitting device according to claim 1, wherein the phosphor includes a compound having formula (17)



wherein

M^1 is Pb, Cu, or any combination thereof;

M^2 is Li, Na, K, Rb, Cs, Au, Ag, or any combination thereof;

M^3 is Be, Mg, Ca, Sr, Ba, Zn, Cd, or any combination thereof;

M^4 is Sc, Y, B, Al, La, Ga, In, or any combination thereof;

M^5 is Si, Ti, Zr, Mn, V, Nb, Ta, W, Mo, or any combination thereof;

M^6 is Bi, Sn, Pr, Sm, Eu, Gd, Dy, or any combination thereof;

X is F, Cl, Br, I, or any combination thereof;

$$0 < a \leq 2;$$

$$0 \leq b \leq 2;$$

$$0 \leq c \leq 10;$$

$$0 < d \leq 10;$$

$$0 \leq e \leq 14;$$

$$0 \leq f \leq 14;$$

$$0 \leq g \leq 10;$$

$$0 \leq h \leq 2;$$

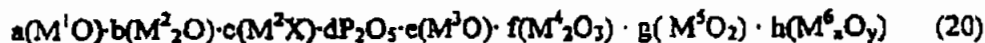
$$1 \leq o \leq 2;$$

$$1 \leq p \leq 5;$$

$$1 \leq x \leq 2; \text{ and}$$

$$1 \leq y \leq 5.$$

8. The light emitting device according to claim 1, wherein the phosphor includes a compound having formula (20)



wherein

M^1 is Pb, Cu, or any combination thereof;

M^2 is Li, Na, K, Rb, Cs, Au, Ag, or any combination thereof;

M^3 is Be, Mg, Ca, Sr, Ba, Zn, Cd, Mn, or any combination thereof;

M^4 is Sc, Y, B, Al, La, Ga, In, or any combination thereof;

M^5 is Si, Ge, Ti, Zr, Hf, V, Nb, Ta, W, Mo, or any combination thereof;

M^6 is Bi, Sn, Pr, Sm, Eu, Gd, Dy, Ce, Tb, or any combination thereof,

X is F, Cl, Br, I, or any combination thereof,

$0 < a \leq 2$;

$0 \leq b \leq 12$;

$0 \leq c \leq 16$;

$0 < d \leq 3$;

$0 \leq e \leq 5$;

$0 \leq f \leq 3$;

$0 \leq g \leq 2$;

$0 < h \leq 2$;

$1 \leq x \leq 2$; and

$1 \leq y \leq 5$.

9. The light emitting device according to any one of the claims 1 to 8, wherein the phosphor includes one or more single compounds or any combination thereof.

10. The light emitting device according to any one of the claims 1 to 9 further comprising a sealing material configured to cover the light emitting diode and the phosphor.

11. The light emitting device according to claim 10, wherein the phosphor is distributed in the sealing material.

12. The light emitting device according to any one of the claims 1 to 11, wherein the phosphor is mixed with a hardening material.

13. The light emitting device according to any one of the claims 1 to 12, wherein the light emitting diode comprises a plurality of light emitting diodes.

14. The light emitting device according to any one of the claims 1 to 13, further comprising electrically conductive paste provided between the light emitting diode and the one of the plurality of electrodes.

15. The light emitting device according to any one of the claims 1 to 14, further comprising a reflector configured to reflect the light from the light emitting diode.