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(54) **COLOR STABLE RED-EMITTING PHOSPHORS**

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(57) **ABSTRACT**

A process for preparing a Mn^{+4} doped phosphor of formula I

$$A_x[MF_y]:Mn^{+4} \qquad I$$

includes gradually adding a first solution to a second solution gradually discharging the product liquor from the reactor while volume of the product liquor in the reactor remains constant;

wherein

A is Li, Na, K, Rb, Cs, or a combination thereof;

M is Si, Ge, Sn, Ti, Zr, Al, Ga, In, Sc, Y, La, Nb, Ta, Bi, Gd, or a combination thereof;

x is the absolute value of the charge of the $[MF_y]$ ion;

y is 5, 6 or 7.

The first solution includes a source of M and HF and the second solution includes a source of Mn to a reactor in the presence of a source of A.

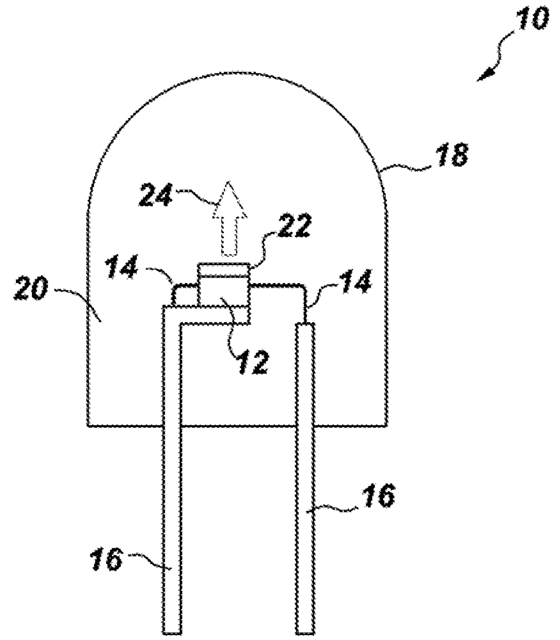
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Fig. 1

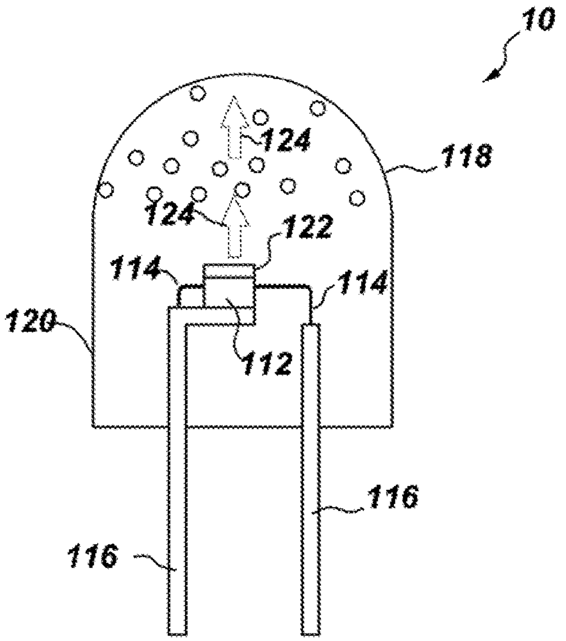
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Fig. 2

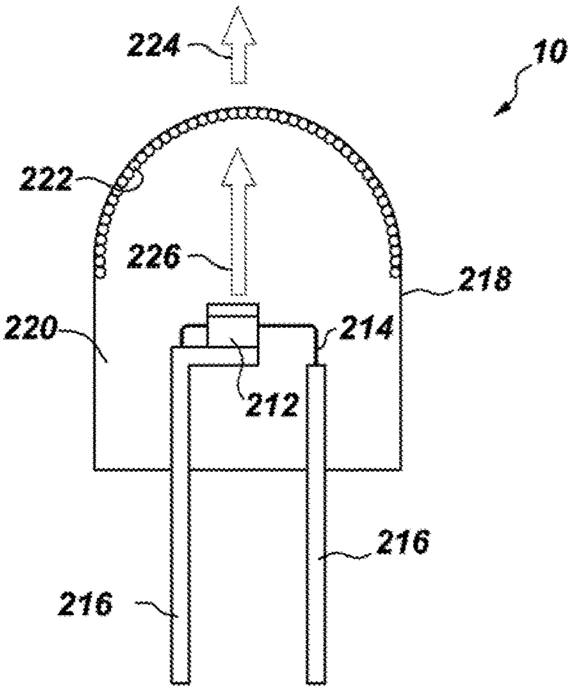

Fig. 3

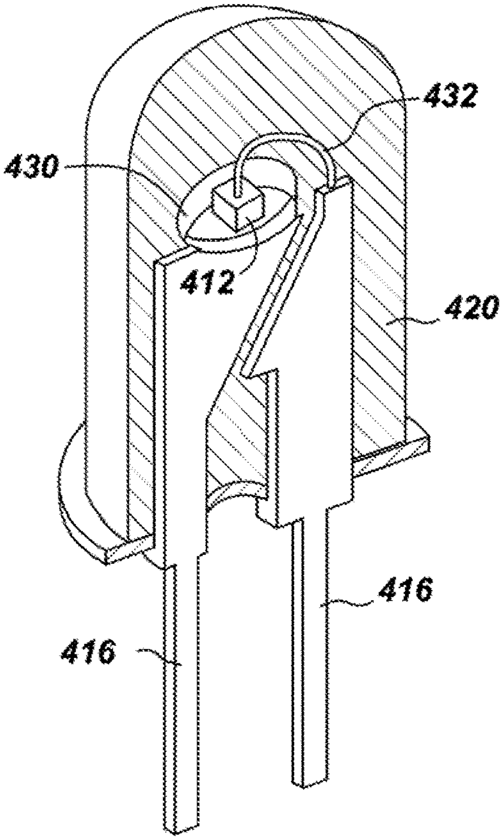

Fig. 4

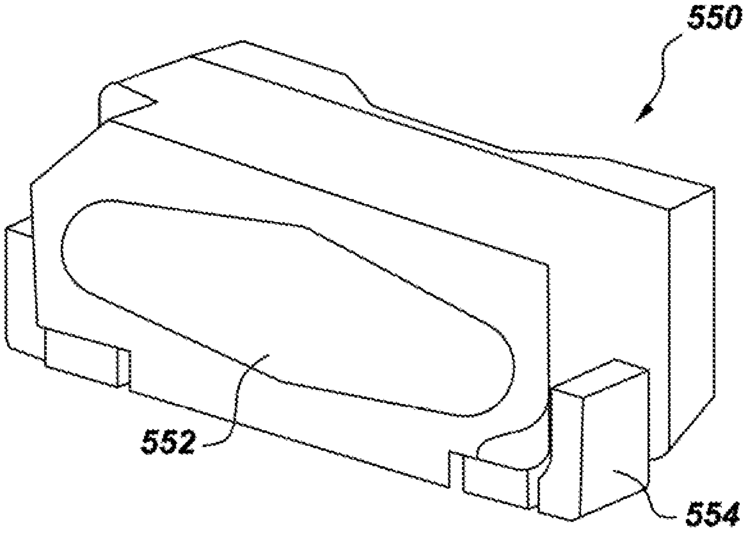

Fig. 5

COLOR STABLE RED-EMITTING PHOSPHORS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a non-provisional of and claims priority from U.S. provisional application, Ser. No. 62/118,703, filed Feb. 20, 2015, the entire disclosure of which is incorporated herein by reference.

BACKGROUND

[0002] Red-emitting phosphors based on complex fluoride materials activated by Mn^{4+}, such as those described in U.S. Pat. No. 7,358,542, U.S. Pat. No. 7,497,973, and U.S. Pat. No. 7,648,649, can be utilized in combination with yellow/green emitting phosphors such as YAG:Ce to achieve warm white light (CCTs<5000 K on the blackbody locus, color rendering index (CRI)>80) from a blue LED, equivalent to that produced by current fluorescent, incandescent and halogen lamps. These materials absorb blue light strongly and efficiently emit in a range between about 610 nm and 658 nm with little deep red/NIR emission. Therefore, luminous efficacy is maximized compared to red phosphors that have significant emission in the deeper red where eye sensitivity is poor. Quantum efficiency can exceed 85% under blue (440-460 nm) excitation. In addition, use of the red phosphors for displays can yield high gamut and efficiency.

[0003] Processes for preparing the materials described in the patent and scientific literature typically involve mixing the raw materials and precipitating the product. Some examples of such batch processes are described in Paulusz, A. G., J. Electrochem. Soc., 942-947 (1973), U.S. Pat. No. 7,497,973, and U.S. Pat. No. 8,491,816. However, scale-up issues and batch to batch variation of properties of the product can be a significant problem. Moreover, batch processes produce materials having a broad range of particles sizes including relatively large particles. Large particles may clog dispensing equipment, causing problems in manufacturing LED packages, and also tend to settle unevenly, resulting in, non homogeneous distribution. Therefore, processes for preparing the red phosphor that can yield a product having a smaller median particle size and a narrower particle size distribution, and allow better control over the final properties of the product, while maintaining performance in lighting and display applications, are desirable.

BRIEF DESCRIPTION

[0004] Briefly, in one aspect, the present invention relates to processes for synthesizing a Mn^{4+} doped phosphor of formula I

$$A_x[MF_y]:Mn^{+4} \qquad \text{I}$$

[0005] wherein

[0006] A is Li, Na, K, Rb, Cs, or a combination thereof;

[0007] M is Si, Ge, Sn. Ti, Zr, Al, Ga, In, Sc, Y, La, Nb, Ta, Bi, Gd, or a combination thereof;

[0008] x is the absolute value of the charge of the $[MF_y]$ ion; and

[0009] y is 5, 6 or 7.

[0010] The process includes gradually adding a first solution comprising a source of M and HF and a second solution comprising a source of Mn to a reactor in the presence of a source of A, to form a product liquor comprising the Mn^{+4} doped phosphor; and gradually discharging the product liquor from the reactor; wherein volume of the product liquor in the reactor remains constant.

[0011] In another aspect, the present invention relates to Mn^{4+} doped phosphors of formula I.

DRAWINGS

[0012] These and other features, aspects, and advantages of the present invention will become better understood when the following detailed description is read with reference to the accompanying drawings in which like characters represent like parts throughout the drawings, wherein:

[0013] FIG. **1** is a schematic cross-sectional view of a lighting apparatus in accordance with one embodiment of the invention;

[0014] FIG. **2** is a schematic cross-sectional view of a lighting apparatus in accordance with another embodiment of the invention;

[0015] FIG. **3** is a schematic cross-sectional view of a lighting apparatus in accordance with yet another embodiment of the invention;

[0016] FIG. **4** is a cutaway side perspective view of a lighting apparatus in accordance with one embodiment of the invention;

[0017] FIG. **5** is a schematic perspective view of a surface-mounted device (SMD) backlight LED.

DETAILED DESCRIPTION

[0018] The Mn^{4+} doped phosphors of formula I are complex fluoride materials, or coordination compounds, containing at least one coordination center, surrounded by fluoride ions acting as ligands, and charge-compensated by counter ions as necessary. For example, K_2SiF^6:Mn^{+4}, the coordination center is Si and the counterion is K. Complex fluorides are occasionally written as a combination of simple, binary fluorides but such a representation does not indicate the coordination number for the ligands around the coordination center. The square brackets (occasionally omitted for simplicity) indicate that the complex ion they encompass is a new chemical species, different from the simple fluoride ion. The activator ion (Mn^{4+}) also acts as a coordination center, substituting part of the centers of the host lattice, for example, Si. The host lattice (including the counter ions) may further modify the excitation and emission properties of the activator ion.

[0019] In particular embodiments, the coordination center of the phosphor, that is, M in formula I, is Si, Ge, Sn, Ti, Zr, or a combination thereof. More particularly, the coordination center is Si, Ge, Ti, or a combination thereof, and the counterion, or A in formula I, is Na, K, Rb, Cs, or a combination thereof, and y is 6. Examples of phosphors of formula I include Examples of phosphors of formula I include $K_2[SiF_6]:Mn^{4+}$, $K_2[TiF_6]:Mn^{4+}$, $K_2[SnF_6]:Mn^{4+}$, $Cs_2[TiF_6]$, $Rb_2[TiF_6]$, $Cs_2[SiF_6]$, $Rb_2[SiF_6]$, $Na_2[TiF_6]:Mn^{4+}$, $Na_2[ZrF_6]:Mn^{4+}$, $K_3[ZrF_7]:Mn^{4+}$, $K_3[BiF_6]:Mn^{4+}$, $K_3[YF_6]:Mn^{4+}$, $K_3[LaF_6]:Mn^{4+}$, $K_3[GdF_6]:Mn^{4+}$, $K_3[NbF_7]:Mn^{4+}$, $K_3[TaF_7]:Mn^{4+}$. In particular embodiments, the phosphor of formula I is $K_2SiF_6:Mn^{4+}$.

[0020] The amount of manganese in the Mn^{+4} doped phosphors of formula I may range from about 1.2 mol % (about 0.3 wt %) to about 16.5 mol % (about 4 wt %). In particular embodiments, the amount of manganese may range from about 2 mol % (about 0.5 wt %) to 13.4 mol % (about 3.3 wt %), or from about 2 mol % to 12.2 mol % (about 3 wt %), or from about 2 mol % to 11.2 mol % (about 2.76 wt %), or from about 2 mol % to about 10 mol % (about 2.5 wt %), or from about 2 mol % to 5.5 mol % (about 1.4 wt %), or from about 2 mol % to about 3.0 mol % (about 0.75 wt %).

[0021] A process according to the present invention includes gradually adding a first solution that contains aqueous HF and a source of M and a second solution that contains a source of Mn to a reactor in the presence of a source of A. Volume of the product liquor in the reactor is maintained at an equilibrium level by discharging the product liquor at about the same rate that feed solutions are added to the reactor. Feed solutions include at least the first and second solutions, along with other solutions that may be added to the reactor before or during the discharging. In some embodiments, the feed solutions may be added to the reactor during an initial period when the reactor is filled to an equilibrium volume without discharging the product liquor. The equilibrium volume is the volume that remains constant while the product liquor is discharged, and is approximately equal to the amount of feed solutions that are added to the reactor in five minutes, particularly in three minutes, more particularly in two minutes, and even more particularly in one minute. The equilibrium volume may be less than 35% of the total volume of all feed solutions, particularly less than 25% of the total volume of all feed solutions, and more particularly less than 15% of the total volume of all feed solutions. In embodiments where the total amount of feed solution is about 1000 ml, the equilibrium volume may range from about 70-200 ml, particularly from about 100-150 mi. Volume of the product liquor remains constant from the time that discharging of the product liquor begins until the discharging is discontinued, or until addition of all feeds is complete or otherwise discontinued. After discharging has begun, the rate of discharge is approximately the same as the total rate of addition of all feeds into the reactor so that the volume of the product liquor remains approximately constant during the discharge period. In the context of the present invention, 'remains approximately constant' means that the volume of the product liquor varies less than about 50% over the time period when the product liquor is being discharged, particularly about 20%, and more particularly about 10%.

[0022] The reaction time, that is, the length of the addition and discharge periods, is not critical. In some embodiments, it may range from about one hour to about two hours. In some embodiments, the feed rates may be set to produce about 10 g product per minute. The feed rate, discharge rate, and equilibrium volume may be chosen so that residence time of the product phosphor in the reactor ranges from about 5 seconds to about 10 minutes, particularly from about 30 seconds to about 5 minutes, more particularly about 30 seconds to about 2 minutes, even more particularly about one minute.

[0023] In some embodiments, the reactor may be precharged with a material selected from HF, a source of A, preformed particles of the Mn^{+4} doped phosphor, or a combination thereof. A non-solvent or antisolvent for the phosphor product may also be included in the precharge. Suitable materials for the antisolvent include acetone, acetic acid, isopropanol, ethanol, methanol, acetonitrile, dimethyl formamide, or a combination thereof. Alternatively, the antisolvent may be included in any of the feed solutions, or in a separate feed solution without a source of M or Mn, particularly in a feed solution that includes a source of A without a source of M or Mn.

[0024] A process according to the present invention may minimize the amount of raw materials used to prepare the phosphors of formula I. In particular, the amount of toxic materials such as HF used may be significantly reduced in comparison with a batch process. Where the amount of HF is reduced, the product liquor may contain a higher level of raw materials compared to a batch process. In many embodiments, the product liquor contains at least 10% dissolved solids, particularly at least 19% dissolved solids, after the start of the discharge. In addition, product yields may be higher compared batch processes. For example, product yield from processes according to the present invention may be as high as 85-95%, whereas yields from batch processes are typically in the range of 60%-75%.

[0025] The first solution includes aqueous HF and a source of M. The source of M may be a compound containing Si, having good in solubility in the solution, for example, H_2SiF_6, Na_2SiF_6, $(NH_4)_2SiF_6$, Rb_2SiF_6, Cs_2SiF_6, SiO_2 or a combination thereof, particularly H_2SiF_6. Use of H_2SiF_6 is advantageous because it has very high solubility in water, and it contains no alkali metal element as an impurity. The source of M may be a single compound or a combination of two or more compounds. The HF concentration in the first solution may be at least 25 wt %, particularly at least 30 wt %, more particularly at least 35 wt %. Water may be added to the first solution, reducing the concentration of HF, to decrease particle size and improve product yield. Concentration of the material used as the source of M may be ≤25 wt %, particularly ≤15 wt %.

[0026] The second solution includes a source of Mn, and may also include aqueous HF as a solvent. Suitable materials for use as the source of Mn include for example, K_2MnF_6, $KMnO_4$, $K_2\ MnCl_6$, MnF_4, MnF_3, MnF_2, MnO_2,and combinations thereof, and, in particular, K_2MnF_6. Concentration of the compound or compounds used as the source of Mn is not critical; and is typically limited by its solubility in the solution. The HF concentration in the second solution may be at least 20 wt %, particularly at least 40 wt %.

[0027] The first and second solutions are added to the reactor in the presence of a source of A while stirring the product liquor. Amounts of the raw materials used generally correspond to the desired composition, except that an excess of the source of A may be present. Flow rates may be adjusted so that the sources of M and Mn are added in a roughly stoichiometric ratio while the source of A is in excess of the stoichiometric amount. In many embodiments, the source of A is added in an amount ranging from about 150% to 300% molar excess, particularly from about 175% to 300% molar excess. For example, in Mn-doped K_2SiF_6, the stoichiometric amount of K required is 2 moles per mole of Mn-doped K_2SiF_6, and the amount of KF or KHF_2 used ranges from about 3.5 moles to about 6 moles of the product phosphor.

[0028] The source of A may be a single compound or a mixture of two or more compounds. Suitable materials include KF, KHF_2, KOH, KCl, KBr, KI, $KOCH_3$ or K_2CO_3, particularly KF and KHF_2, more particularly KHF_2. A source of Mn that contains K, such as K_2MnF_8, may be a K source, particularly in combination with KF or KHF_2. The source of A may be present in either or both of the first and second solutions, in a third solution added separately, in the reactor pot, or in a combination of one or more of these.

[0029] After the product liquor is discharged from the reactor, the Mn^{+4} doped phosphor may be isolated from the product liquor by simply decanting the solvent or by filtration, and treated as described in U.S. Pat. No. 8,252,613 or US 2015/0054400, with a concentrated solution of a compound of formula II in aqueous hydrofluoric acid;

$$A^1_x[MF_y] \tag{II}$$

wherein

[0030] A^1 is H, Li, Na, K, Rb, Cs, or a combination thereof;

[0031] M is Si, Ge, Sn, Ti, Zr, Al, Ga, In, Sc, Y, La, Nb, Ta, Bi, Gd, or a combination thereof;

[0032] x is the absolute value of the charge of the $[MF_y]$ ion; and

[0033] y is 5, 6 or 7.

The compound of formula II includes at least the MF_y anion of the host compound for the product phosphor, and may also include the A cation of the compound of formula I. For a product phosphor of formula Mn-doped K_2SiF_6, suitable materials for the compound of formula II include H_2SiF_6, Na_2SiF, $(NH_4)_2SiF$, Rb_2SiF_6. Cs_2SiF_6, or a combination thereof, particularly H_2SiF_6, K_2SiF_6 and combinations thereof, more particularly K_2SiF_6. The treatment solution is a saturated or nearly saturated of the compound of formula II in hydrofluoric acid. A nearly saturated solution contains about 1-5% excess aqueous HF added to a saturated solution. Concentration of HF in the solution ranges from about 25% (wt/vol) to about 70% (wt/vol), in particular from about 40% (wt/vol) to about 50% (wt/vol). Less concentrated solutions may result in reduced performance of the phosphor. The amount of treatment solution used ranges from about 2-30 ml/g product, particularly about 5-20 ml/g product, more particularly about 5-15 ml/g product.

[0034] The treated phosphor may be vacuum filtered, and washed with one or more solvents to remove HF and unreacted raw materials. Suitable materials for the wash solvent include acetic acid and acetone, and combinations thereof.

[0035] Span is a measure of the width of the particle size distribution curve for a particulate material or powder, and is defined according to equation (1):

$$\text{Span} = \frac{(D_{90} - D_{10})}{D_{50}} \tag{1}$$

wherein

[0036] D_{50} is the median particle size for a volume distribution;

[0037] D_{90} is the particle size for a volume distribution that is greater than the particle size of 90% of the particles of the distribution; and

[0038] D_{10} is the particle size for a volume distribution that is greater than the particle size of 10% of the particles of the distribution.

Particle size of the phosphor powder may be conveniently measured by laser diffraction methods, and software provided with commercial instruments can generate D_{90}. D_{10}, and D_{50} particle size values and span of the distribution. For phosphor particles of the present invention, D_{50} particle size ranges from about 10 μm to about 40 μm, particularly from about 15 μm to about 35 μm, more particularly from about 20 μm to about 30 μm. Span of the particle size distribution may be ≤1.0, particularly ≤0.9, more particularly ≤0.8, and even more particularly ≤0.7. Particle size may be controlled by adjusting flow rates, reactant concentrations, and equilibrium volume of the product liquor.

[0039] After the product phosphor is isolated from the product liquor, treated and dried, it may be annealed to improve stability as described in U.S. Pat. No. 8,906,724. In such embodiments, the product phosphor is held at an elevated temperature, while in contact with an atmosphere containing a fluorine-containing oxidizing agent. The fluorine-containing oxidizing agent may be F_2, HF, SF_6, BrF_5, NH_4HF_2, NH_4F, KF, AlF_3, SbF_5, ClF_3, BrF_3, KrF_2, XeF_2, XeF_4, NF_3, SiF_4, PbF_2, ZnF_2, SnF_2, CdF_2 or a combination thereof. In particular embodiments, the fluorine-containing oxidizing agent is F_2. The amount of oxidizing agent in the atmosphere may be varied to obtain the color stable phosphor, particularly in conjunction with variation of time and temperature. Where the fluorine-containing oxidizing agent is F_2, the atmosphere may include at least 0.5% F_2, although a lower concentration may be effective in some embodiments. In particular the atmosphere may include at least 5% F_2 and more particularly at least 20% F_2. The atmosphere may additionally include nitrogen, helium, neon, argon, krypton, xenon, in any combination with the fluorine-containing oxidizing agent. In particular embodiments, the atmosphere is composed of about 20% F_2 and about 80% nitrogen.

[0040] The temperature at which the phosphor is contacted with the fluorine-containing oxidizing agent is any temperature in the range from about 200° C. to about 700° C., particularly from about 350° C. to about 600° C. during contact, and in some embodiments from about 500° C. to about 600° C. The phosphor is contacted with the oxidizing agent for a period of time sufficient to convert it to a color stable phosphor. Time and temperature are interrelated, and may be adjusted together, for example, increasing time while reducing temperature, or increasing temperature while reducing time. In particular embodiments, the time is at least one hour, particularly for at least four hours, more particularly at least six hours, and most particularly at least eight hours.

[0041] After holding at the elevated temperature for the desired period of time, the temperature in the furnace may be reduced at a controlled rate while maintaining the oxidizing atmosphere for an initial cooling period. After the initial cooling period, the cooling rate may be controlled at the same rate or a different rate, or may be uncontrolled. In some embodiments, the cooling rate is controlled at least until a temperature of 200° C. is reached. In other embodiments, the cooling rate is controlled at least until a temperature at which it is safe to purge the atmosphere is reached. For example, the temperature may be reduced to about 50° C. before a purge of the fluorine atmosphere begins. Reducing the temperature at a controlled rate of ≤5° C. per minute may yield a phosphor product having superior properties compared to reducing the temperature at a rate of ≤10° C./minute. In various embodiments, the rate may be controlled at ≤5° C. per minute, particularly at ≤3° C. per minute, more particularly at a rate of ≤1° C. per minute.

[0042] The period of time over which the temperature is reduced at the controlled rate is related to the contact temperature and cooling rate. For example, when the contact temperature is 540° C. and the cooling rate is 10° C./minute, the time period for controlling the cooling rate may be less than one hour, after which the temperature may be allowed to fall to the purge or ambient temperature without external control. When the contact temperature is 540° C. and the cooling rate is ≤5° C. per minute, then the cooling time may be less than two hours. When the contact temperature is 540'C and the cooling rate is ≤3° C. per minute, then the cooling time may be less than three hours. When the contact temperature is 540° C. and the cooling rate is ≤1° C. per minute, then the cooling time is may be less than four hours. For example, the temperature may be reduced to about 200° C. with controlled cooling, then control may be discontinued. After the controlled cooling period, the temperature may fall at a higher or lower rate than the initial controlled rate.

[0043] The manner of contacting the phosphor with the fluorine-containing oxidizing agent is not critical and may be accomplished in any way sufficient to convert the phosphor to a color stable phosphor having the desired properties. In some embodiments, the chamber containing the phosphor may be dosed and then sealed such that an overpressure develops as the chamber is heated, and in others, the fluorine and nitrogen mixture is flowed throughout the anneal process ensuring a more uniform pressure. In some embodiments, an additional dose of the fluorine-containing oxidizing agent may be introduced after a period of time.

[0044] The annealed phosphor may be treated with a saturated or nearly saturated solution of a composition of formula II in aqueous hydrofluoric acid, as described in U.S. Pat. No. 8,252,613. The amount of treatment solution used ranges from about 10 ml/g product to 20 ml/g product, particularly about 10 ml/g product. The treated annealed phosphor may be isolated by filtration, washed with solvents such as acetic acid and acetone to remove contaminates and traces of water, and stored under nitrogen.

[0045] Any numerical values recited herein include all values from the lower value to the upper value in increments of one unit provided that there is a separation of at least 2 units between any lower value and any higher value. As an example, if it is stated that the amount of a component or a value of a process variable such as, for example, temperature, pressure, time and the like is, for example, from 1 to 90, preferably from 20 to 80, more preferably from 30 to 70, it is intended that values such as 15 to 85, 22 to 68, 43 to 51, 30 to 32 etc. are expressly enumerated in this specification. For values which are less than one, one unit is considered to be 0.0001, 0.001, 0.01 or 0.1 as appropriate. These are only examples of what is specifically intended and all possible combinations of numerical values between the lowest value and the highest value enumerated are to be considered to be expressly stated in this application in a similar manner.

[0046] A lighting apparatus or light emitting assembly or lamp **10** according to one embodiment of the present invention is shown in FIG. **1**. Lighting apparatus **10** includes a semiconductor radiation source, shown as light emitting diode (LED) chip **12**, and leads **14** electrically attached to the LED chip. The leads **14** may be thin wires supported by a thicker lead frame(s) **16** or the leads may be self-supported electrodes and the lead frame may be omitted. The leads **14** provide current to LED chip **12** and thus cause it to emit radiation.

[0047] The lamp may include any semiconductor blue or UV light source that is capable of producing white light when its emitted radiation is directed onto the phosphor. In one embodiment, the semiconductor light source is a blue emitting LED doped with various impurities. Thus, the LED may comprise a semiconductor diode based on any suitable III-V, II-VI or IV-IV semiconductor layers and having an emission wavelength of about 250 to 550 nm. In particular, the LED may contain at least one semiconductor layer comprising GaN, ZnSe or SiC. For example, the LED may comprise a nitride compound semiconductor represented by the formula $In_iGa_jAl_kN$ (where $0\leq i$; $0\leq j$; $0\leq k$ and $I+j+k=1$) having an emission wavelength greater than about 250 nm and less than about 550 nm. In particular embodiments, the chip is a near-uv or blue emitting LED having a peak emission wavelength from about 400 to about 500 nm. Such LED semiconductors are known in the art. The radiation source is described herein as an LED for convenience. However, as used herein, the term is meant to encompass all semiconductor radiation sources including, e.g., semiconductor laser diodes. Further, although the general discussion of the exemplary structures of the invention discussed herein is directed toward inorganic LED based light sources, it should be understood that the LED chip may be replaced by another radiation source unless otherwise noted and that any reference to semiconductor, semiconductor LED, or LED chip is merely representative of any appropriate radiation source, including, but not limited to, organic light emitting diodes.

[0048] In lighting apparatus **10**, phosphor composition **22** is radiationally coupled to the LED chip **12**. Radiationally coupled means that the elements are associated with each other so radiation from one is transmitted to the other. Phosphor composition **22** is deposited on the LED **12** by any appropriate method. For example, a water based suspension of the phosphor(s) can be formed, and applied as a phosphor layer to the LED surface. In one such method, a silicone slurry in which the phosphor particles are randomly suspended is placed around the LED. This method is merely exemplary of possible positions of phosphor composition **22** and LED **12**. Thus, phosphor composition **22** may be coated over or directly on the light emitting surface of the LED chip **12** by coating and drying the phosphor suspension over the LED chip **12**. In the case of a silicone-based suspension, the suspension is cured at an appropriate temperature. Both the shell **18** and the encapsulant **20** should be transparent to allow white light **24** to be transmitted through those elements. Although not intended to be limiting, in some embodiments, the median particle size of the phosphor composition ranges from about 1 to about 50 microns, particularly from about 15 to about 35 microns.

[0049] In other embodiments, phosphor composition **22** is interspersed within the encapsulant material **20**, instead of being formed directly on the LED chip **12**. The phosphor (in the form of a powder) may be interspersed within a single region of the encapsulant material **20** or throughout the entire volume of the encapsulant material. Blue light emitted by the LED chip **12** mixes with the light emitted by phosphor composition **22**, and the mixed light appears as white light. If the phosphor is to be interspersed within the material of encapsulant **20**, then a phosphor powder may be added to a polymer or silicone precursor, loaded around the LED chip **12**, and then the polymer precursor may be cured to solidify the polymer or silicone material. Other known phosphor interspersion methods may also be used, such as transfer loading.

[0050] In some embodiments, the encapsulant material **20** is a silicone matrix having an index of refraction R, and, in addition to phosphor composition **22**, contains a diluent material having less than about 5% absorbance and index of refraction of R±0.1. The diluent material has an index of refraction of ≤1.7, particularly ≤1.6, and more particularly ≤1.5. In particular embodiments, the diluent material is of formula II, and has an index of refraction of about 1.4. Adding an optically inactive material to the phosphor/silicone mixture may produce a more gradual distribution of light flux through the phosphor/encapsulant mixture and can result in less damage to the phosphor. Suitable materials for the diluent include fluoride compounds such as LiF, MgF_2, CaF_2, SrF_2, AlF_3, K_2NaAlF_6, $KMgF_3$, $CaLiAlF_6$, K_2LiAlF_6, and K_2SiF_6, which have index of refraction ranging from about 1.38 (AlF_3 and K_2NaAlF_6) to about 1.43 (CaF_2), and polymers having index of refraction ranging from about 1.254 to about 1.7. Non-limiting examples of polymers suitable for use as a diluent include polycarbonates, polyesters, nylons, polyetherimides, polyetherketones, and polymers derived from styrene, acrylate, methacrylate, vinyl, vinyl acetate, ethylene, propylene oxide, and ethylene oxide monomers, and copolymers thereof, including halogenated and unhalogenated derivatives. These polymer powders can be directly incorporated into silicone encapsulants before silicone curing.

[0051] In yet another embodiment, phosphor composition **22** is coated onto a surface of the shell **18**, instead of being formed over the LED chip **12**. The phosphor composition is preferably coated on the inside surface of the shell **18**, although the phosphor may be coated on the outside surface of the shell, if desired. Phosphor composition **22** may be coated on the entire surface of the shell or only a top portion of the surface of the shell. The UV/blue light emitted by the LED chip **12** mixes with the light emitted by phosphor composition **22**, and the mixed light appears as white light. Of course, the phosphor may be located in any two or all three locations or in any other suitable location, such as separately from the shell or integrated into the LED.

[0052] FIG. **2** illustrates a second structure of the system according to the present invention. Corresponding numbers from FIGS. **1**-**4** (e.g. **12** in FIGS. **1** and **112** in FIG. **2**) relate to corresponding structures in each of the figures, unless otherwise stated. The structure of the embodiment of FIG. **2** is similar to that of FIG. **1**, except that the phosphor composition **122** is interspersed within the encapsulant material **120**, instead of being formed directly on the LED chip **112**. The phosphor (in the form of a powder) may be interspersed within a single region of the encapsulant material or throughout the entire volume of the encapsulant material. Radiation (Indicated by arrow **126**) emitted by the LED chip **112** mixes with the light emitted by the phosphor **122**, and the mixed light appears as white light **124**. If the phosphor is to be interspersed within the encapsulant material **120**, then a phosphor powder may be added to a polymer precursor, and loaded around the LED chip **112**. The polymer or silicone precursor may then be cured to solidify the polymer or silicone. Other known phosphor interspersion methods may also be used, such as transfer molding.

[0053] FIG. **3** illustrates a third possible structure of the system according to the present invention. The structure of the embodiment shown in FIG. **3** is similar to that of FIG. **1**, except that the phosphor composition **222** is coated onto a surface of the envelope **218**, instead of being formed over the LED chip **212**. The phosphor composition **222** is preferably coated on the inside surface of the envelope **218**, although the phosphor may be coated on the outside surface of the envelope, if desired. The phosphor composition **222** may be coated on the entire surface of the envelope, or only a top portion of the surface of the envelope. The radiation **226** emitted by the LED chip **212** mixes with the light emitted by the phosphor composition **222**, and the mixed light appears as white light **224**. Of course, the structures of FIGS. **1**-**3** may be combined, and the phosphor may be located in any two or all three locations, or in any other suitable location, such as separately from the envelope, or integrated into the LED.

[0054] In any of the above structures, the lamp may also include a plurality of scattering particles (not shown), which are embedded in the encapsulant material. The scattering particles may comprise, for example, alumina or titania. The scattering particles effectively scatter the directional light emitted from the LED chip, preferably with a negligible amount of absorption.

[0055] As shown in a fourth structure in FIG. **4**, the LED chip **412** may be mounted in a reflective cup **430**. The cup **430** may be made from or coated with a dielectric material, such as alumina, titania, or other dielectric powders known in the art, or be coated by a reflective metal, such as aluminum or silver. The remainder of the structure of the embodiment of FIG. **4** is the same as those of any of the previous figures, and can include two leads **416**, a conducting wire **432**, and an encapsulant material **420**. The reflective cup **430** is supported by the first lead **416** and the conducting wire **432** is used to electrically connect the LED chip **412** with the second lead **416**.

[0056] Another structure (particularly for backlight applications) is a surface mounted device ("SMD") type light emitting diode **550**, e.g. as illustrated in FIG. **5**. This SMD is a "side-emitting type" and has a light-emitting window **552** on a protruding portion of a light guiding member **554**. An SMD package may comprise an LED chip as defined above, and a phosphor material that is excited by the light emitted from the LED chip. Other backlight devices include, but are not limited to, TVs, computers, smartphones, tablet computers and other handheld devices that have a display including a semiconductor light source; and a color stable Mn^{4+} doped phosphor according to the present invention.

[0057] When used with an LED emitting at from 350 to 550 nm and one or more other appropriate phosphors, the resulting lighting system will produce a light having a white color. Lamp **10** may also include scattering particles (not shown), which are embedded in the encapsulant material. The scattering particles may comprise, for example, alumina or titania. The scattering particles effectively scatter the directional light emitted from the LED chip, preferably with a negligible amount of absorption.

[0058] In addition to the color stable Mn^{+4} doped phosphor, phosphor composition **22** may include one or more other phosphors. When used in a lighting apparatus in combination with a blue or near UV LED emitting radiation in the range of about 250 to 550 nm, the resultant light emitted by the assembly will be a white light. Other phosphors such as green, blue, yellow, red, orange, or other color phosphors may be used in the blend to customize the white color of the resulting light and produce specific spectral power distributions. Other materials suitable for use in phosphor composition **22** include electroluminescent polymers such as polyfluorenes, preferably poly(9,9-dioctyl fluorene) and copolymers thereof, such as poly(9,9'-dioctylfluorene-co-bis-N,N'-(4-butylphenyl)diphenylamine) (F8-TFB); poly(vinylcarbazole) and polyphenylenevinylene and their derivatives. In addition, the light emitting layer may include a blue, yellow, orange, green or red phosphorescent dye or metal complex, or a combination thereof. Materials suitable for use as the phosphorescent dye include, but are not limited to, tris(1-phenylisoquinoline) iridium (III) (red dye), tris(2-phenylpyridine) iridium (green dye) and Indium (III) bis(2-(4,6-difluorephenyl)pyridinato-N,C2) (blue dye). Commercially available fluorescent and phosphorescent metal complexes from ADS (American Dyes Source, Inc.) may also be used. ADS green dyes include ADS060GE, ADS061GE, ADS063GE, and ADS066GE, ADS078GE, and ADS090GE. ADS blue dyes include ADS064BE, ADS065BE, and ADS070BE. ADS red dyes include ADS067RE, ADS068RE, ADS069RE, ADS075RE, ADS076RE, ADS067RE, and ADS077RE.

[0059] Suitable phosphors for use in phosphor composition **22** in addition to the $Mn^{4'+}$ doped phosphor include, but are not limited to:

$((Sr_{1-z}(Ca, Ba, Mg, Zn)_z)_{1-(x+w)}(Li, Na, K, Rb)_wCe_x)_3(Al_{1-y}Si_y)O_{4+y+3(x-w)}F_{1-y-3(x-w)}$, wherein $0<x\leq0.10$, $0\leq y\leq0.5$, $0\leq z\leq0.5$, $0\leq w\leq x$;

$(Ca, Ce)_3Sc_2Si_3O_{12}$ (CaSiG);

$(Sr,Ca,Ba)_3Al_{1-x}Si_xO_{4+x}F_{1-x}:Ce^{3+}$ (SASOF));

$(Ba,Sr,Ca)_5(PO_4)_3(Cl,F,Br,OH):Eu^{2+},Mn^{2+}$; $(Ba,Sr.Ca)BPO_5:Eu^{2+},Mn^{2+}$; $(Sr,Ca)_{10}(PO_4)_6{*}\square B_2O_3:Eu^{2+}$ (wherein $0<\square\leq1$);

$Sr_2Si_3O_8{*}2SrCl_2:Eu^{2+}$; $(Ca,Sr,Ba)_3MgSi_2O_8:Eu^{2+},Mn^{2+}$; $BaAl_8O_{13}:Eu^{2+}$;

$2SrO{*}0.84P_2O_5{*}0.16B_2O_3:Eu^{2+}$; $(Ba,Sr,Ca)MgAl_{10}O_{17}:Eu^{2+},Mn^{2+}$; $(Ba,Sr,Ca)Al_2O_4:Eu^{2+}$;

$(Y,Gd,Lu,Sc,La)BO_3:Ce^{3+},Tb^{3+}$; $ZnS:Cu^+,Cl^-$; $ZnS:Cu^+,Al^{3+}$; $ZnS:Ag^+,Cl^-$; $ZnS:Ag^+,Al^{3+}$;

$(Ba,Sr,Ca)_2Si_{1-\square}O_{4-2\square}:Eu^{2+}$ (wherein $-0.2\leq\square\leq0.2$); $(Ba,Sr,Ca)_2(Mg,Zn)Si_2O_7:Eu^{2+}$;

$(Sr,Ca,Ba)(Al,Ga,In)_2S_4:Eu^{2+}$; $(Y,Gd,Tb,La,Sm,Pr,Lu)_3(Al,Ga)_{5-\square}O_{12-3/2\square}:Ce^{3+}$ (wherein $0\leq\square\leq0.5$);

$(Y,Gd,Lu,Tb)_3(Al,Ga)_5O_{12}:Ce^{3+}$;

$(Ca,Sr)_8(Mg,Zn)(SiO_4)_4Cl_2:Eu^{2+},Mn^{2+}$; $Na_2Gd_2B_2O_7:Ce^{3+},Tb^{3+}$; $(Sr,Ca,Ba,Mg,Zn)_2P_2O_7:Eu^{2+},Mn^{2+}$;

$(Gd,Y,Lu,La)_2O_3:Eu^{3+},Bi^{3+}$; $(Gd,Y,Lu,La)_2O_2S:Eu^{3+},Bi^{3+}$; $(Gd,Y,Lu,La)VO_4:Eu^{3+},Bi^{3+}$;

$(Ca,Sr)S:Eu^{2+},Ce^{3+}$; $SrY_2S_4:Eu^{2+}$; $CaLa_2S_4:Ce^{3+}$; $(Ba,Sr,Ca)MgP_2O_7:Eu^{2+},Mn^{2+}$;

$(Y,Lu)_2WO_6:Eu^{3+},Mo^{6+}$; $(Ba,Sr,Ca)_\square Si_\square N_\square:Eu^{2+}$ (wherein $2\square+4\square=3\square$);

$(Ba,Sr,Ca)_2Si_{5-x}Al_xN_{8-x}O_x:Eu^{2+}$ (wherein $0\leq x\leq2$); $Ca_3(SiO_4)Cl_2:Eu^{2+}$;

$(Lu,Sc,Y,Tb)_{2-u-v}Ce_vCa_{t+u}Li_wMg_{2-w}P_w(Si,Ge)_{3-w}O_{12-u/2}$ (where $-0.5\leq u\leq1$, $0<v\leq0.1$, and $0\leq w\leq0.2$);

$(Y,Lu,Gd)_{2-\square}Ca_\square Si_4N_{6+\square}C_{1-\square}:Ce^{3+}$, (wherein $0\leq\square\leq0.5$);

α-SiAlON doped with Eu^{2+} and/or Ce^{3+}; $(Ca,Sr,Ba)SiO_2N_2:Eu^{2+},Ce^{3+}$;

β-SiAlON:Eu^{2+}, $3.5MgO{*}0.5MgF_2{*}GeO_2:Mn^{4+}$; $(Sr,Ca,Ba,Mg)AlSiN_3:Eu^{2+}$;

$(Sr,Ca,Ba)_3SiO_5:Eu^{2+}$; $Ca_{1-c-f}Ce_cEu_fAl_{1+c}Si_{1-c}N_3$, (where $0\leq c\leq0.2$, $0\leq f\leq0.2$);

$Ca_{1-h-r}Ce_hEu_rAl_{1-h}(Mg,Zn)_hSiN_3$, (where $0\leq h\leq0.2$, $0\leq r\leq0.2$);

$Ca_{1-2s-t}Ce_5(Li,Na)_5Eu_tAlSiN_3$, (where $0\leq s\leq0.2$, $0\leq f\leq0.2$, $s+t>0$); and

$Ca_{1-\square-\square-\phi}Ce_\square(Li,Na)_\square Eu_\square Al_{1+\square-\square}Si_{1-\square+\square}N_3$, (where $0\leq\square\leq0.2$, $0\leq\square\leq0.4$, $0\leq\square\leq0.2$).

[0060] In particular, phosphor composition **22** may include one or more phosphors that result in a green spectral power distribution under ultraviolet, violet, or blue excitation. In the context of the present invention, this is referred to as a green phosphor or green phosphor material. The green phosphor may be a single composition or a blend that emits light in a green to yellow-green to yellow range, such as cerium-doped yttrium aluminum garnets, more particularly $(Y,Gd,Lu,Tb)_3(Al,Ga)_5O_{12}:Ce^{3+}$. The green phosphor may also be a blend of blue- and red-shifted garnet materials. For example, a Ce^{3+}-doped garnet having blue shifted emission may be used in combination with a Ce^{3+}-doped garnet that has red-shifted emission, resulting in a blend having a green spectral power distribution. Blue- and red-shifted garnets are known in the art. In some embodiments, versus a baseline $Y_3Al_5O_{12}:Ce^{3+}$ phosphor, a blue-shifted garnet may have Lu^{3+} substitution for Y^{3+}, Ga^{3+} substitution for Al^{3+}, or lower Ce^{3+} doping levels in a $Y_3Al_5O_{12}:Ce^{3+}$ phosphor composition. A red-shifted garnet may have Gd^{3+}/Tb^{3+} substitution for Y^{3+} or higher Ce^{3+} doping levels. An example of a green phosphor that is particularly useful for display application is β-SiAlON.

[0061] The ratio of each of the individual phosphors in the phosphor blend may vary depending on the characteristics of the desired light output. The relative proportions of the individual phosphors in the various embodiment phosphor blends may be adjusted such that when their emissions are blended and employed in an LED lighting device, there is produced visible light of predetermined x and y values on the CIE chromaticity diagram. As stated, a white light is preferably produced. This white light may, for instance, may possess an x value in the range of about 0.20 to about 0.55, and a y value in the range of about 0.20 to about 0.55. As stated, however, the exact identity and amounts of each phosphor in the phosphor composition can be varied according to the needs of the end user. For example, the material can be used for LEDs intended for liquid crystal display (LCD) backlighting. In this application, the LED color point would be appropriately tuned based upon the desired white, red, green, and blue colors after passing through an LCD/color filter combination. The list of potential phosphor for blending given here is not meant to be exhaustive and these Mn^{4+}-doped phosphors can be blended with various phosphors with different emission to achieve desired spectral power distributions.

[0062] In some embodiments, lighting apparatus **10** has a color temperature less than or equal to 4200° K, and phosphor composition **22** includes a red phosphor consisting of a color stable Mn^{4+} doped phosphor of formula I. That is, the only red phosphor present in phosphor composition **22** is the color stable Mn^{+4} doped phosphor, in particular, the phosphor is $K_2SiF_6:Mn^{4+}$. The composition may additionally include a green phosphor. The green phosphor may be a C^{3+}-doped garnet or blend of garnets, particularly a Ce^{3+}-doped yttrium aluminum garnet, and more particularly, YAG having the formula $(Y,Gd,Lu,Tb)_3(Al,Ga)_5O_{12}:Ce^{3+}$. When the red phosphor is $K_2SiF_6:Mn^{4+}$, the mass ratio of the red phosphor to the green phosphor material may be less than 3.3, which may be significantly lower than for red phosphors of similar composition, but having lower levels of the Mn dopant.

[0063] The color stable Mn^{+4} doped phosphors of the present invention may be used in applications other than those described above. For example, the material may be used as a phosphor in a fluorescent lamp, in a cathode ray tube, in a plasma display device or in a liquid crystal display (LCD). The material may also be used as a scintillator in an electromagnetic calorimeter, in a gamma ray camera, in a computed tomography scanner or in a laser. These uses are merely exemplary and not limiting.

EXAMPLES

Comparative Examples 1 and 2: Preparation of Mn^{+4} Doped K_2SiF_6 by Batch Process

[0064] Amounts and distribution of starting materials among Beakers A-C are shown in Table 1. Beaker A was stirred aggressively, and the contents of beaker B were added thereto dropwise over the course of about five minutes. Dropwise addition of the contents of beaker C to beaker A was started about one minute after the contents of beaker B was started and continued over the course of about four minutes. The precipitate was digested for 5 minutes and the stirring was stopped. The supernatant was decanted, and the precipitate was vacuum filtered, rinsed once with acetic acid and twice with acetone, and then dried under vacuum. The dried powder was sifted through a 170-mesh screen, and annealed under a 20% F_2/80% nitrogen atmosphere for 8 hour at 540° C. The annealed phosphor was washed with a solution of 49% HF saturated with K_2SiF_6, dried under vacuum and sifted through a 170-mesh screen.

TABLE 1

Batch Process Raw Materials

Comp. Ex. no.	Solution A KF (g)	KH$_2$F (g)	K$_2$MnF$_6$ (g)	HF (49%) (mL)	Solution B H$_2$SiF$_6$ (35%) (mL)	HF (49%) (mL)	Solution C K$_2$MnF$_6$ (g)	HF (49%) (mL)
1 070913AT		8.1	0.18	65	1.5	60	0.18	21
2 071213AT		16.2	0.37	130	30	120	0.37	42

Examples 1-6: Preparation of Mn^{4+} Doped K_2SiF_6 by Continuous Flow Process

Procedure

[0065] A 2000 ml separatory funnel used as a reaction vessel was stirred at a rate of about 300 RPM. Three peristaltic pumps were used to maintain tight control over all flow rates. Flow rates were set between 15-40 mL/min for solution A and solution B and between 30-100 mL/min for solution **3**. Amounts and distribution of starting materials among Solutions A-C for Examples 1-6 are shown in Table 2.

[0066] The reaction vessel was filled to an equilibrium volume of 100-200 mL and then the stopcock was opened such that the combined flow rate of the three flows was equal to the flow rate out of the drain. The volume in the reaction vessel was maintained within about 5-10% of the initial equilibrium volume from the time the reaction vessel started to drain until the reaction was complete. The combined flow rate of the three solutions ranged from 80-130 mL/minute. The residence time of the product phosphor in the reaction vessel ranged from 30 seconds to 2 minutes.

[0067] The outflow from the reaction vessel was directed to a receiving vessel, where the solvent was decanted from the product. A nearly saturated solution of K_2SiF_6 in 49% HF was prepared by adding 4.2 g K_2SiF_6 per 100 ml 49% HF to form a suspension which was vacuum filtered to remove excess solids. Approximately 2 vol % 49% HF was added to the saturated solution, to form a nearly saturated solution. The slurry was mixed with 500 ml of the nearly saturated at a rate of about 6 ml solution per 1 g product and stirred for about 20 minutes. The treated product was vacuum filtered, rinsed once with acetic acid and three times with acetone, and then dried under vacuum. The dried powder was sifted through a 170-mesh screen, and annealed under an atmosphere composed of 20% F_2/80% nitrogen for about 8 hours at 540° C. The slurry was mixed with 1000 ml of a solution of 49% HF nearly saturated with K_2SiF_6 at a rate of about 12 ml solution per 1 g product and stirred for about 20 minutes. The treated product was vacuum filtered, rinsed once with acetic acid and three times with acetone, and then dried under vacuum. The dried powder was sifted through a 170-mesh screen, and annealed under an atmosphere composed of 20% F_2/80% nitrogen for about 8 hours at 540° C.

TABLE 2

	Solution A			Solution B		Solution C		
Example no.	KF (g)	KH$_2$F (g)	HF (49%) (mL)	K$_2$MnF$_6$ (g)	HF (49%) (mL)	H$_2$SiF$_6$ (35%) (mL)	HF (49%) (mL)	H$_2$SiF$_6$: HF Ratio
1	24		63	3.3	55	27	70	1:2.5
2 C072215B-T		34	51	3	50	28	56	1:2.0
3 F061715A-T		31	63	2.5	42	2	0	1:0
4 F061715B-T		31	63	2.5	42	28	70	1:2.5
5 F061715C-T		31	63	2.5	42	28	35	1:1.25
6 C092215A-TGAT		149.6	264	12	202	112	240	1:2.14

TABLE 2-continued

	Solution A			Solution B		Solution C		
Example no.	KF (g)	KH_2F (g)	HF (49%) (mL)	K_2MnF_6 (g)	HF (49%) (mL)	H_2SiF_6 (35%) (mL)	HF (49%) (mL)	H_2SiF_6: HF Ratio
7 C092215B-TGAT		151.8	268	13.2	218	108.3	232	1:2.14
8 C092215C-TGAT		120.6	181	16	240	105	225	1:2.14

[0068] Sample tapes were prepared by mixing 500 mg of the phosphor with 1.50 g Sylgard 184 silicone. The mixture was degassed in a vacuum chamber for about 15 minutes. The mixture (0.70 g) was poured into a disc-shaped template (28.7 mm diameter and 0.79 mm thick) and baked for 30 minutes at 90° C. The sample was cut into squares of size approximately 5 mm×5 mm for testing.

[0069] QE of the phosphors was measured at excitation wavelength of 450 nm QE of the phosphors was measured at excitation wavelength of 450 nm and is reported relative to a reference sample of Mn^{4+} doped K_2SiF_6 with 0.68% Mn and a particle size of 28 microns from a commercial source. Lifetime was determined using an Edinburgh FS900 Spectrometer by fitting a single exponential decay to the measured data between 1.4 ms and 67 ms after excitation. Particle size data was obtained using a Horiba LA-960 Laser Scattering Particle Size Distribution Analyzer. The amount of manganese incorporated in the phosphor was determined by inductively coupled plasma mass spectrometry (ICP-MS), and is reported as weight %, based on total weight of the phosphor material. Results are shown in Table 3.

TABLE 3

Example no.	QE, %	Lifetime	D_{10}, μm	D_{50}, μm	D_{90}, μm	Span	Mn, %
Comp. ex. 1	103.8	8.540	15	29	50	1.20	0.84
Comp. ex. 2	103.4	NA	11	43	78	1	0.56
1	100.2	8.391	21	31	44	0.74	2.55
2	103.1	8.445	14	22	33	0.86	1.34
3	49.5	6.900	10	15	23	0.87	1.73
4	100.5	8.388	18	27	40	0.81	2.1
5	92.5	8.205	10	15	22	0.80	1.86
6	101.1	8.408	21	29	39	0.64	2.35
7	99.7	8.37	22	33	49	0.81	2.58
8	99.7	8.322	23	32	42	0.59	3.06

[0070] For Comparative Examples 1 and 2, it can be seen that particle size and span increased at the larger scale; D_{10}, D_{50}, and D_{90} increased by 21%-25%, and the span of the distribution increased from 1.20 to 1.54. In contrast, for the phosphors of Examples 1-6, span was dramatically narrower than for the batch samples, ranging between 0.74 and 0.87, with D_{50} ranging between 15 μm and 31 μm. For Examples 3 and 5, QE of the phosphors was reduced compared to that of the phosphors of Examples 1, 2, and 4, which used higher amounts of HF in the process. Examples 6-8 demonstrate that a narrow particle size distribution can be achieved at higher dopant levels.

[0071] While only certain features of the invention have been illustrated and described herein, many modifications and changes will occur to those skilled in the art. It is, therefore, to be understood that the appended claims are intended to cover all such modifications and changes as fall within the true spirit of the invention.

1-10. (canceled)

11. A Mn^{+4} doped phosphor of formula I comprising a population of particles having a particle size distribution comprising D_{50} particle size ranging from about 10 μm to about 40 μm and a span less than 1.1;

$$A_x[MF_y]:Mn^{+4} \qquad \text{I}$$

wherein

A is Li, Na, K, Rb, Cs, or a combination thereof;

M is Si, Ge, Sn, Ti, Zr, Al, Ga, In, Sc, Y, La, Nb, Ta, Bi, Gd, or a combination thereof;

x is the absolute value of the charge of the $[MF_y]$ ion; and

y is 5, 6 or 7.

12. A Mn^{+4} doped phosphor according to claim **11**, wherein the D_{50} ranges from about 15 μm to about 35 μm.

13. A Mn^{+4} doped phosphor according to claim **11**, wherein the span is less than 1.

14. A Mn^{+4} doped phosphor according to claim **11**, wherein the span is less than 0.9.

15. A Mn^{+4} doped phosphor according to claim **11**, wherein the span is less than 0.8.

16. A lighting apparatus comprising a Mn^{+4} doped phosphor according to claim **11**.

17. A backlight device comprising a Mn^{+4} doped phosphor according to claim **11**.

18-22. (canceled)

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