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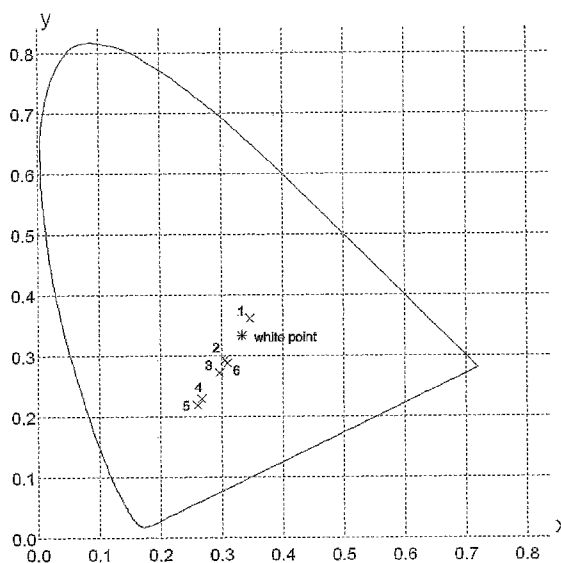
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(54) Title: WHITE-LIGHT EMITTING PHOSPHOR



(57) Abstract: The invention concerns a phosphor excitable by ultraviolet radiation, wherein the phosphor contains Dy³⁺ and Tm³⁺ and devices using such a phosphor.

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White-light emitting phosphor

Field of the Invention

The present invention relates to a phosphor which is excitable by ultraviolet radiation and
5 to light-emitting devices using this phosphor.

Background of the Invention

Human beings interpret quite differently visual stimuli as the colour "white". Not only
broad-band emissions like the ones from daylight sources produce a "white" colour
10 perception, but also narrow band light sources like fluorescent tubes. These tubes are
glass tubes filled with mercury vapour and electrodes at each end. The interior of such a
tube is coated with a fluorescent material consisting of a phosphor. The fluorescent
material absorbs most of the ultraviolet (UV) part of the mercury (Hg) emission(s) and
shows broad band luminescence mainly in the red part of the visible spectrum. The white-
15 light produced in a fluorescent tube is a combination of the visible emission of mercury at
368 nm, 408 nm and 439 nm and the luminescence of the coating.

In recent years, there has been a growing concern about mercury which eventually
pollutes the environment because it is demonstrably a health hazard. Therefore, there has
20 been an increasing demand for light-emitting devices that are operated without mercury.

White-light fluorescent tubes that are operated without mercury demand a phosphor that
emits light intensively and can deliver white-light with high efficiency directly through UV-
excitation of the phosphor in the coating.

25

It is therefore an object of the present invention to provide an ultraviolet-excitable white-
light emitting phosphor that has excellent light-emitting properties and can deliver white-
light.

30 Summary of the Invention

It is known that rare-earth ions which are doped into solid host materials can give rise to
sharp emissions in a certain region of the visible spectrum. For example, $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ is one
of the most efficient red phosphors.

Rare-earth ions other than Eu^{3+} have their emissions at different wavelengths. For example, yttrium-aluminium borate (YAB) and yttrium-aluminium-scandium borate are suitable hosts for rare-earth ions. YAB forms uniaxial crystals of huntite type in space group R32 with three formula units per unit cell. Such crystals consist of layered
 5 arrangements of alternating BO_3^{3-} triangles and metal ion layers along the $\langle 001 \rangle$ direction, which coincides with the crystallographic c-axis. The Y^{3+} ions are located in trigonal prismatic sites with D_3 symmetry. They are co-ordinated to three oxygens from the borate top and bottom layers, respectively, where the two oxygen triangles are slightly rotated (8.3°) against each other. Upon doping, rare-earth ions replace yttrium ions.

10

In the quest for a material which shows rare-earth emission in the visible range such that this emission stimulates a white colour perception, the inventors have produced dozens of doped YAB crystals containing different combinations and amounts of rare-earth ions.

15 Among these many samples those systems which contained Tm^{3+} and Dy^{3+} simultaneously in the proper ratio were the only ones showing the desired effect of emitting white-light upon UV-excitation. Thereby, the white light is produced by the rare-earth ions via a down-conversion mechanism. The rare-earth ions absorb electromagnetic energy in the UV-band and convert it to light in the visible spectrum (Tm^{3+} : blue, Dy^{3+} :
 20 yellow) and lattice phonons (warmth). It is emphasised that for such phosphors the white impression results from luminescence of the rare-earth ions only and does not require the presence of mercury emission bands.

The desired white colour can also be obtained when using host materials other than YAB,
 25 for instance, lutetium-aluminium-borates or lutetium-aluminium-scandium borates. Other suitable host materials are for example transparent amorphous materials which are doped with Tm^{3+} and Dy^{3+} ions, e.g. glasses.

According to the invention, a phosphor excitable by ultraviolet radiation is composed of a
 30 host material containing dysprosium and thulium with oxidation number 3, e.g. a dysprosium (Dy^{3+}) and thulium (Tm^{3+}) containing rare-earth yttrium-aluminium-scandium borate or yttrium-aluminium-borate that is represented by the general formula $(\text{Y}_{1-x-y}\text{Tm}_x\text{Dy}_y)\text{Al}_{3-z}\text{Sc}_z(\text{BO}_3)_4$, wherein $0 < (x+y) \leq 1$, $0 \leq z \leq 3$. Preferably, x is in the range 0.03

$\leq x \leq 0.05$ and y is in the range $0.03 \leq y \leq 0.05$. These compounds are highly stable and, correspondingly, phosphors based on such compounds have a long lifetime.

Alternatively, instead of crystalline inorganic host materials other highly stable host materials may be used, for example, a transparent glass doped with the same rare-earth ions. In this and other cases, the host material preferably contains about 0.5 to 3.5 weight percent Dy^{3+} and about 0.5 to 3.5 weight percent Tm^{3+} .

When using a phosphor according to the invention, a white luminescent lamp can be provided in which excitation by ultraviolet light that is radiated by a discharge medium is converted to cause efficient emission within the visible wavelength range of 451 nm to 579 nm, which emission is interpreted as white-light by the human eye. The discharge medium may be a noble gas. E.g., the noble gas may be xenon gas.

The features mentioned above will become evident from the following description which illustrates examples of the present invention.

Brief Description of the Drawings

Fig. 1 is a graph showing the x, y coordinates of the examples 1 to 6 in the CIE

(Commission Internationale d'Eclairage) 1931 x, y chromaticity diagram;

Fig. 2 is a graph showing a comparison of the relationship between the emitted intensities of the phosphors and the corresponding colour temperature for examples 1 to 5 of the present invention.

Description of preferred embodiments

As described above, as a result of continued research and development, the inventors of the present invention have succeeded in discovering a material which has superior light-emission characteristics and emits light perceived as white-light by the human eye, in particular an ultraviolet-excitable phosphor that is composed of thulium and dysprosium activated rare-earth aluminium-scandium borate that is represented by the general formula $(\text{Y}_{1-x-y}\text{Tm}_x\text{Dy}_y)\text{Al}_{3-z}\text{Sc}_z(\text{BO}_3)_4$, wherein $0 < (x+y) \leq 1$ and $0 \leq z \leq 3$.

With regard to a method of producing a phosphor of the present invention, an yttrium compound such as yttrium oxide, a thulium compound such as thulium oxide, a

dysprosium compound such as dysprosium oxide, an aluminium compound such as aluminium oxide, a scandium compound such as scandium oxide, and a boron compound such as boron oxide are first taken as the basic materials of this phosphor. These basic materials are next weighed, collected, and well mixed in accordance with the above-described compositional formula.

These materials are next poured into a heat-resistant receptacle such as a crucible that is composed of alumina, carbon, or platinum, and are subjected to pre-sintering at a temperature of 400 - 600 °C. The materials are next sintered for 3 - 20 hours in air at a temperature of 900 - 1200 °C, and the obtained sintered and compact body is next subjected to pulverization, washing, drying, and sorting to obtain the white-light emitting phosphor of the present invention in a powdered form.

The above-described pre-sintering and main sintering may be carried out in an oxidizing atmosphere. Further, it is possible to subject the phosphor that has been obtained as described above again to sintering and then similarly to the processes of pulverization, washing, drying and sorting to obtain a phosphor which can be excited by UV-radiation.

In an alternative way, the materials are mixed with an excess of a high temperature flux such as an arbitrary mixture of K_2SO_4 and MoO_3 and poured into a heat-resistant receptacle such as a crucible that is composed of alumina, carbon, or platinum, in which the materials are subjected to pre-sintering at a temperature of 400 - 600 °C. In the next step, the materials are subjected to main melting for 2 hours in air at a temperature of 1120 °C and are then cooled down at the rate of 1 °C/hour to 850 °C, and finally cooled down to room temperature. Afterwards, the material is subjected to washing with a strong base such as KOH (8m) in order to obtain an ultraviolet-excitable phosphor in single crystalline form.

Actual examples of ultraviolet-excitable white-light phosphors of the present invention are described in the following.

Example 1

As the raw materials of a phosphor, 1.5968 g of Y_2O_3 , 0.2296 g of Dy_2O_3 , 0.0030 g of Tm_2O_3 , 2.3537 g of Al_2O_3 , 2.1441 g of B_2O_3 , 3.50 g of K_2SO_4 , 9.64 g of MoO_3 are each

weighed and, following uniform mixing, are poured into a crucible made of alumina and subjected to pre-sintering for two hours at 500 °C in air. Then, the temperature is raised to 1120 °C, and after heating for two hours in air, the material is slowly cooled with a rate of 1 °C/hour to obtain crystals of the material in the molten flux. The material is next boiled in
 5 KOH (8m), and the crystals obtained in this way are cleaned, dried, and sorted to obtain a white-light emitting phosphor having a composition of $Y_{0.919}Dy_{0.080}Tm_{0.001}Al_3(BO_3)_4$.

Examples 2 to 5

The ratios among the Y component, Tm component, Al component and Dy component are
 10 modified as appropriate and the processes of, for example, mixing and sintering and crystal growing are carried out under the same conditions as in Example 1 in order to obtain ultraviolet-excitable white-light emitting phosphors having the compositions as shown in Table 1.

15 Table 1: Composition of phosphors according to Examples 1 to 5

Example	Composition
1	$Y_{0.919}Dy_{0.080}Tm_{0.001}Al_3(BO_3)_4$
2	$Y_{0.93}Dy_{0.04}Tm_{0.03}Al_3(BO_3)_4$
3	$Y_{0.91}Dy_{0.04}Tm_{0.05}Al_3(BO_3)_4$
4	$Y_{0.89}Dy_{0.07}Tm_{0.04}Al_3(BO_3)_4$
5	$Y_{0.87}Dy_{0.04}Tm_{0.09}Al_3(BO_3)_4$

Referring to Fig. 1, which is a graph showing the x,y co-ordinates in the 1931 x,y colour space (CIE 1931 x,y chromaticity diagram) of Examples 1 to 6 of the present invention,
 20 and Fig. 2, which is a graph showing a comparison of the relationship between the emitted wavelengths of phosphors by means of colour temperatures, it can be seen that ultraviolet-excitable white-light emitting phosphors according to Examples 1 to 5 have a strong emission intensity and can supply white-light with high efficiency. These phosphors, when irradiated by ultraviolet light having a wavelength of 350 nm or less, can
 25 produce white-light being composed of emission at the wavelengths 451 nm, 455 nm, 470 nm, 474 nm, 481 nm, 485 nm, 564 nm, 567 nm, 571 nm, 574 nm, 579 nm and several peaks in the range of ± 5 nm around these wavelengths with higher efficiency and stronger emitted intensity, having a colour temperature of approximately 4600 - 10000 K.

Therefore, such phosphors can be applied to various types of light-emitting devices that are free from mercury and take a noble gas such as xenon as the excitation source. Such phosphors may be used, for example, for plasma display panels or fluorescent lamps.

5 Example 6

A sodium borosilicate glass with base glass composition $25\text{Na}_2\text{O} - 25\text{B}_2\text{O}_3 - 50\text{SiO}_2$ (numbers represent mol percent), to which 1 weight percent Tm^{3+} as Tm_2O_3 and 1 weight percent Dy^{3+} as Dy_2O_3 are added, is prepared by thoroughly mixing appropriate amounts of the oxides in a mortar. The mixture is placed in a platinum crucible, put into an oven
10 and kept there for one hour at 1100°C . The platinum crucible is shaken in intervals of 15 minutes to obtain a homogeneous melt. After one hour, the melt is cast into a copper mould and the quenched glass left alone to cool down to room temperature.

Similarly to crystalline materials, a Dy^{3+} and Tm^{3+} doped glass obtained in this way emits
15 radiation close to the white-point in the CIE 1931 x,y chromaticity diagram (Fig. 1). In glasses containing dysprosium and thulium broader emission bands appear in the spectral ranges 440 - 465 nm, 465 - 500 nm, and 555 - 600 nm.

Phosphors according to the invention can be used for mercury-free fluorescent lamps,
20 plasma display panels or any other devices, in which ultraviolet radiation needs to be converted to white-light in a highly efficient manner.

Claims

1. A phosphor excitable by ultraviolet radiation, wherein the phosphor contains Dy^{3+} and Tm^{3+} .
- 5 2. A phosphor according to claim 1, wherein the phosphor contains Dy^{3+} in a range of about 0.5 to 3.5 weight percent and Tm^{3+} in a range of about 0.5 to 3.5 weight percent.
3. A phosphor according to claim 1 or 2, wherein the phosphor is an yttrium-aluminium-scandium borate containing dysprosium and thulium.
- 10 4. A phosphor according to claim 1 or 2, wherein the phosphor is an yttrium-aluminium borate containing dysprosium and thulium.
- 15 5. A phosphor according to claim 3 or 4, wherein the phosphor is a crystalline compound having the formula $(\text{Y}_{1-x-y}\text{Tm}_x\text{Dy}_y)\text{Al}_{3-z}\text{Sc}_z(\text{BO}_3)_4$, wherein $0 < (x+y) \leq 1$ and $0 \leq z \leq 3$.
6. A phosphor according to claim 5, wherein $0.03 \leq x \leq 0.05$ and $0.03 \leq y \leq 0.05$.
- 20 7. A phosphor according to claim 1 or 2, wherein Dy^{3+} and Tm^{3+} are embedded in an amorphous matrix.
8. A phosphor according to claim 7, wherein the matrix is a transparent glass.
- 25 9. A phosphor according to claim 8, wherein the glass is a sodium borosilicate glass.
10. A white-light emitting device comprising a phosphor according to any of claims 1 to 9.
11. A white-light emitting device according to claim 10, further comprising an ultraviolet
- 30 radiation emitting source.
12. A white-light emitting device according to claim 11, wherein the ultraviolet radiation emitting source is free from mercury.

13. A white-light emitting device according to claim 12, wherein the ultraviolet radiation emitting source contains a noble gas and means for discharging the noble gas.

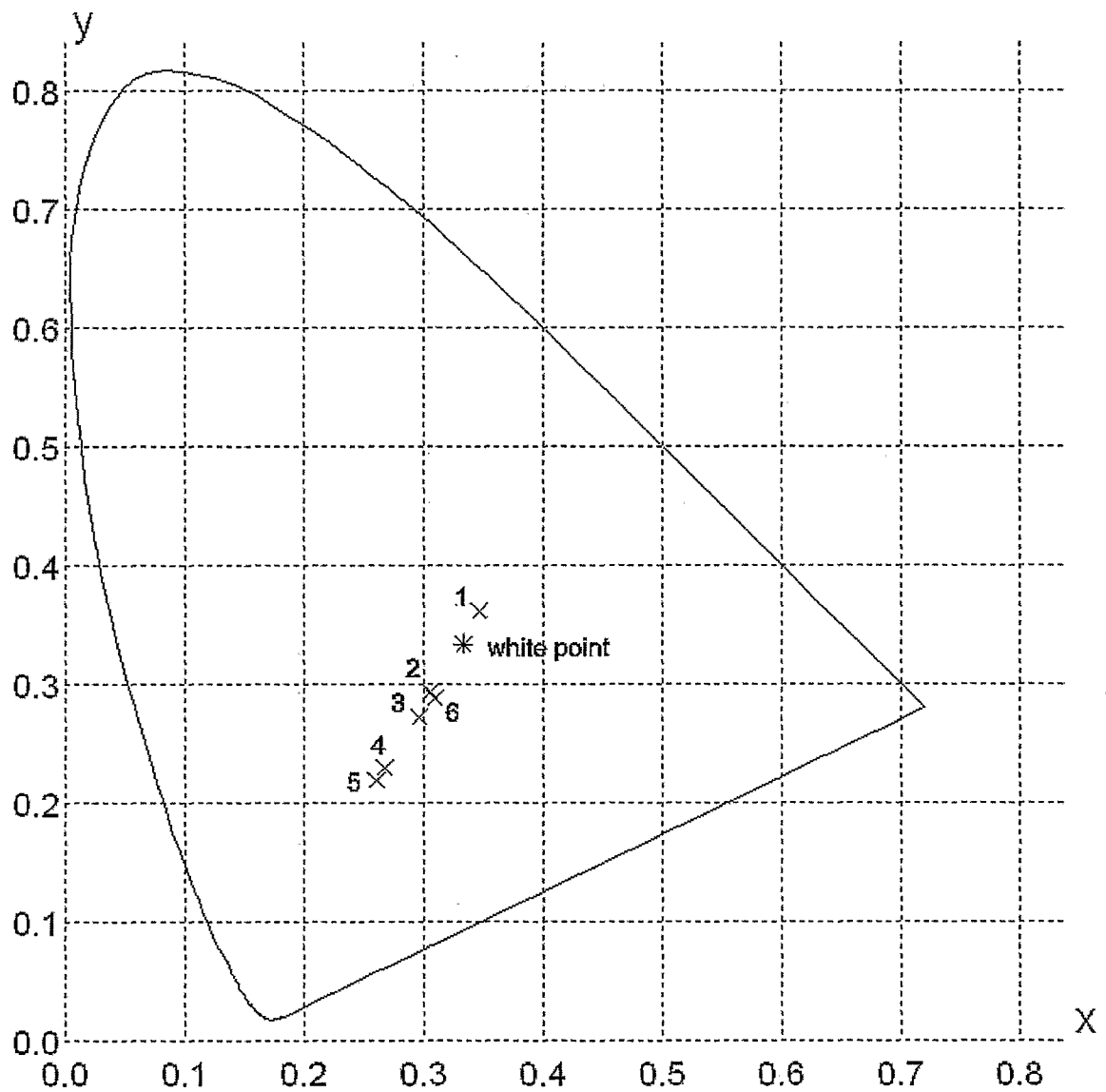
14. A white-light emitting device according to claim 10, wherein the device is a fluorescent
5 lamp.

15. A white light-emitting device according to claim 10, wherein the device is a plasma display panel.

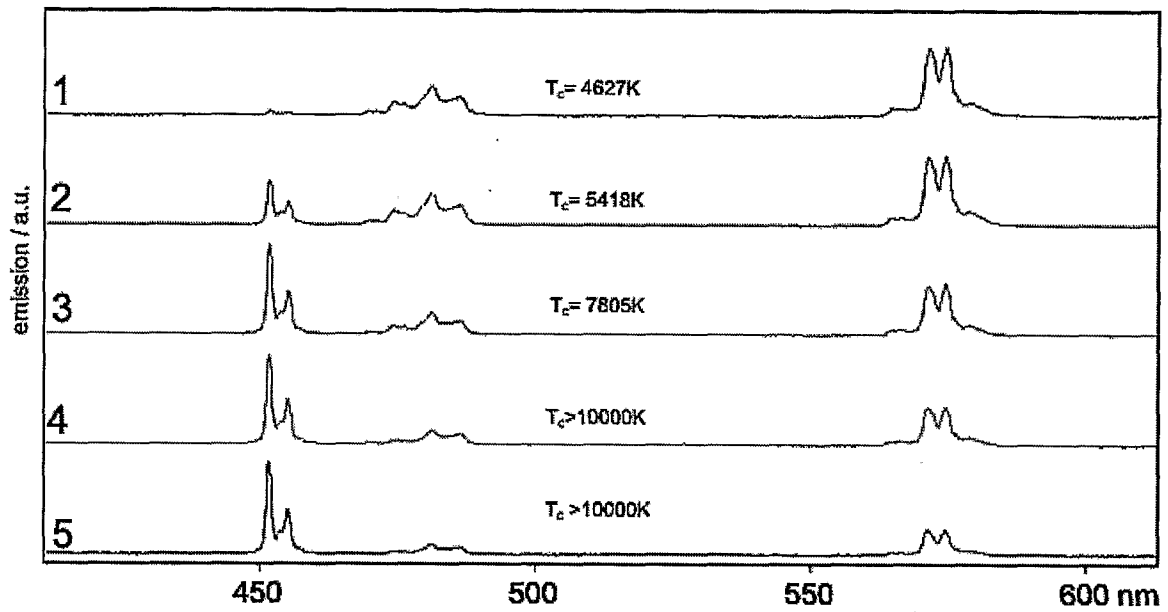
10 16. Use of an ultraviolet excitable phosphor according to any of claims 1 to 9 to convert ultraviolet radiation to white-light close to the white-point in the CIE 1931 x,y chromaticity diagram.

17. Use of an ultraviolet excitable phosphor according to any of claims 1 to 9 in a
15 fluorescent lamp or a plasma display panel.

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Fig. 1

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Fig. 2