

Patent Application Kokai No. 57-168982

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Luminescent material

Claim:

1. A luminescent material to be excited with slow electron beam, characterized by a mixture obtained by blending a phosphor consisting of an oxide expressed by the composition ABO_4 (A is at least one selected from Y and Gd, B is at least one selected from Nb and Ta) containing europium as an activator, with an electric conductive oxide material.

The present invention relates to a novel luminescent material to be excited with slow electron beam which exhibits a red luminescence.

Heretofore, as a commercially available phosphor which emits light with a high brightness by excitation with slow electron beam, self-activating zinc oxide phosphor ($ZnO:Zn$) has been known. This phosphor exhibits a green luminescence by excitation with slow electron beam and is utilized as phosphor for luminescent display tubes such as electric calculators and various measuring instruments.

Recently, a number of phosphors which are activated with transition metal ions or rare earth element ions have been developed. It has long been known in the art that when these metal ions are irradiated with an electron beam, ultraviolet ray or near-infrared ray in a

liquid, bright line emission spectra inherent to the metal ions are observed, and they attracted attentions and have been studied as laser materials. From among these studies, laser materials such as YAG:Nd was put in practical use on one hand and it was also found that cerium, europium, erbium, etc. show luminescence at a high efficiency in various substrate materials. Since then, extensive studies have been conducted regarding phosphors activated with rare earth element ions. As a result, many materials were put in use, among which yttrium oxide, yttrium oxysulfide and yttrium vanadate which are activated with europium are the most important and are used as red components for color television sets, high pressure mercury lamps, etc.

These phosphors emit light with a high brightness when excited with a fast electron beam of several kV, ultraviolet beams or the like. However, these phosphors emit little light when excited with a slow electron beam and accordingly cannot be used as phosphors for luminescent displays. Consequently, only with luminescent display tubes having a green color from the self-activated green luminescent zinc oxide material, and development of bright phosphor materials capable of emitting bright luminescence other than green have been sought for in order to expand the use of the display tubes.

To this end, $Y_2O_3S:Eu$, $ZnS:Ag$, etc. made conductive by In_2O_3 , have been developed but not to the extent that they can be used in display tubes.

The biggest hindrance to the commercial utilization of red luminescence display tubes using $Y_2O_3S:Eu$ phosphor is the decrease in

brightness with lapse of time. This decrease in brightness is said to be caused due to formation of an inactive surface layer on the particles of $Y_2O_3:S:Eu$ phosphor, increase in resistance of the conductive powder such as In_2O_3 , and degradation of the interface between the particles of $Y_2O_3:S:Eu$ and the particles of In_2O_3 . Of these causes, the decrease in brightness due to the formation of the inactive surface layer on the particles of $Y_2O_3:S:Eu$ is not very significant and the increase in resistance of the particles of In_2O_3 can be controlled by the process conditions of production of the conductive powder. On the other hand, the degradation of the interface between the particles of $Y_2O_3:S:Eu$ and the particles of In_2O_3 , which is considered to be the major cause, cannot be avoided because $Y_2O_3:S$ containing S is susceptible to temperature increase by concentrated contact resistance.

More specifically, conductance g of two adjacent particles is formed by a parallel connection of particle contact resistance R_c and particle surface leakage resistance R_f . R_c is a series connection of concentrated resistance $R_s = 1/2rc'H_v$ (H_v = conductance of the body of the particles $[A/Vm]$, and rc' = effective diameter of the contact surface $[m]$) due to the strong convergence of current flux at the contact point and interface resistance $\rho_s/\pi rc'^2$ shown by adsorbed molecular layer in the interface (ρ_s = resistance per unit surface of the interface layer) and expressed by the following equation.

$$R_c = \frac{1}{2rc'2H_v} + \frac{\rho_s}{\pi rc'^2} \quad [V/A]$$

The surface leakage resistance R_f is given by the following formula by surface integration assuming that the surface conductivity is H_f .

$$H_f = \frac{1}{2} n(2r/rc')/\pi H_f$$

Accordingly, the apparent conductivity H_a of phosphor compact is given by the following equation.

$$H_a = \frac{\frac{rc'}{r}}{1 + \frac{2Hv \rho_b}{\pi rc'}} + \frac{\frac{\pi}{2r}}{\ln \frac{2r}{rc'}} H_f$$

For the mixture powder of the particles of $Y_2O_3S:Eu$ and the particles of In_2O_3 , Hv is $10^{-4} \leq Hv \leq 10^{-2} [A/Vcm]$ and the effects from surface resistance and the interface resistance are small. Accordingly, the above equation can be expressed approximately by

$$H_a = \frac{rc'}{r} Hv$$

Assuming that heat conductivity is λ , and potential across the particles is U , the temperature increase at the contact point is expressed by

$$\theta = U^2 / \left(\frac{8 \lambda r}{rc' H_a} \right)$$

If $H_a = 1 [V/Acm]$, $\lambda = 0.2 [W/cm.deg]$ are assumed, we can estimate this value as $0-800^\circ C$ at $U=15V$. For the mixture powder of the particles of $Y_2O_3S:Eu$ and the particles of In_2O_3 , it is said that, due to the presence of sulfur, the contact points are easily deteriorated by heat and the flow of exciting electrons passing through the conductive powder to the anode is hindered and thus the brightness is rapidly decreased with lapse of time.

The present inventor conducted studies on red luminescent oxide phosphors excited by slow electron beam which do not contain sulfur which is otherwise a cause of deterioration and has reached a discovery leading to the present invention that a compound expressed by $ABO_4:Eu$ where A is at least one selected from Y and Gd and B is at least one selected from Nb and Ta) exhibits a red luminescence

with a high brightness. Also, it is found that the effective amount of activator europium is, when converted into Eu_2O_3 , in the range of 10^{-6} - 10^{-1} g per 1 gram of the oxide ABO_4 . Further, it is found that the luminescence threshold voltage of these luminescent materials may be lowered to about 15V by appropriately blending a conductive materials such as In_2O_3 and SnO_2 conductive material. Here, In_2O_3 conductive material means In_2O_3 alone or In_2O_3 doped with tin, germanium, lead or silicon, and SnO_2 conductive material means SnO_2 alone or SnO_2 doped with phosphor, arsenic, antimony or bismuth.

The following are examples of the present invention.

Example 1

$\text{GdNbO}_4:\text{Eu}$ luminescent material was produced in the following process. Gd_2O_3 and Eu_2O_3 were weighed in the ratio of 0.9 mole to 0.1 mole and dissolved in nitric acid. To this solution, aqueous solution of oxalic acid was added to precipitate oxalate, which was then dried and subjected to pyrolysis at 1000°C for 1 hour in the air to obtain $\text{Gd}_2\text{O}_3:\text{Eu}$ (10 m/o). 7.135g of $\text{Gd}_2\text{O}_3:\text{Eu}$, 5.316g of Nb_2O_5 and 13g of Li_2SO_4 were blended in a ball mill and reacted at 1000°C for 16 hours in N_2 . The product was fired in the air for one hour. The resulting product was washed and $\text{GdNbO}_4:\text{Eu}$ was obtained.

As conductive powder, SnO_2 doped with 1% of Sb was used. This powder was prepared by dissolving 1g of tin oxalate and 10mg of Sb in terms of SnO_2 and Sb_2O_3 , and then drying and firing at 1000°C in the air.

2g of SnO_2 was blended to 8g of $\text{GdNbO}_4:\text{Eu}$ and, after thorough drying, 30mg of the mixture was sampled and mounted on a demountable device shown in Fig.1.

In this figure, the luminescent material 4 is mounted on the anode

5 supported by the insulator support 6 placed in the vacuum chamber 1. After evacuating the inside of this demountable device to 1×10^{-6} Torr, the oxide coated filament 2 was activated to generate hot electrons 3 at a filament current of 0.09 mA and a voltage in the range of 0-150 V. Luminescence was observed from about 15 V and a brightness of about 40 Ft.L was obtained at 50 V. The relationship between the brightness (Br), anode current (Ib) and anode voltage (Eb) is shown in Fig. 2 and the luminescence spectrum at that time is shown in Fig.3.

YNbO_4 : Eu, GdTbO_4 :Eu and YTbO_4 :Eu had spectra almost the same as Fig. 3 except for the variation of the relative intensity.

Example 2

YTbO_4 :Eu luminescent material was produced in the following process. Y_2O_3 and Eu_2O_3 were weighed in the ratio of 0.95 mole to 0.05 mole and dissolved in nitric acid.

To this solution, aqueous solution of oxalic acid was added to precipitate oxalate, which was then dried and subjected to pyrolysis at 1000 °C for 1 hour in the air to obtain Y_2O_3 :Eu(5m/o). 4.52g of Y_2O_3 :Eu, 8.84g of Ta_2O_5 and 13g of LiCl were blended in a ball mill and reacted at 1000 °C for 20 hours in N_2 . The resulting product was washed and YTbO_4 :Eu was obtained.

As conductive powder, In_2O_3 doped with Sn was used. This powder was prepared by adding 10g of In_2O_3 to an aqueous solution containing 0.2g of Sn ions in terms of SnO_2 , drying and firing at 1000 °C in the air.

2g of In_2O_3 was added to 8g of YTbO_4 :Eu and after thorough drying 30mg of the mixture was sampled and excited in accordance with Example 1. Red luminescence was observed from about 25V and a

brightness of about 25 Ft.L was obtained at 50V.

Example 3

$\text{YNbO}_4:\text{Eu}$ prepared by a process similar to Examples 1 and 2 was blended with $\text{SnO}_2:\text{Sb}$ and this luminescence material was mounted on the demountable device shown in Fig.1 and was caused to emit continuous direct current luminescence. The brightness was 40Ft.L at 50V. With the conventional $\text{Y}_2\text{O}_3:\text{S:Eu}$, the brightness decreases to 50% or less after about 100 hours as shown in Fig. 4. In contrast, the present invention preserved 90 % of the initial brightness after about 5000 hours as shown in Fig.4. This is attributed to the fact that there is no deterioration at the contact interface of the phosphor with the the conductive particles particles.

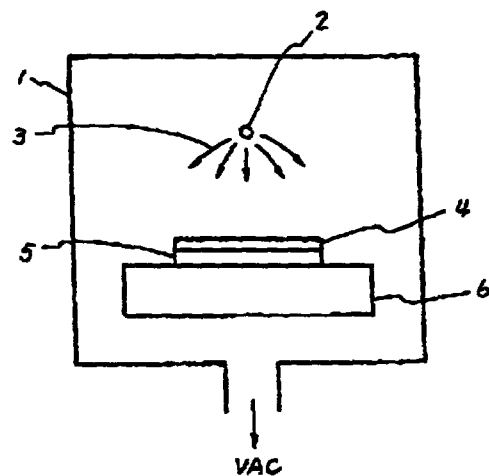
From the foregoing, the present invention provides a red luminescent material which is capable of emitting luminescence at low threshold voltage and is stable for long period of time and accordingly is very advantageous in commercializing red display tubes.

は発光材料、5は陽極、6は絶縁基板である。

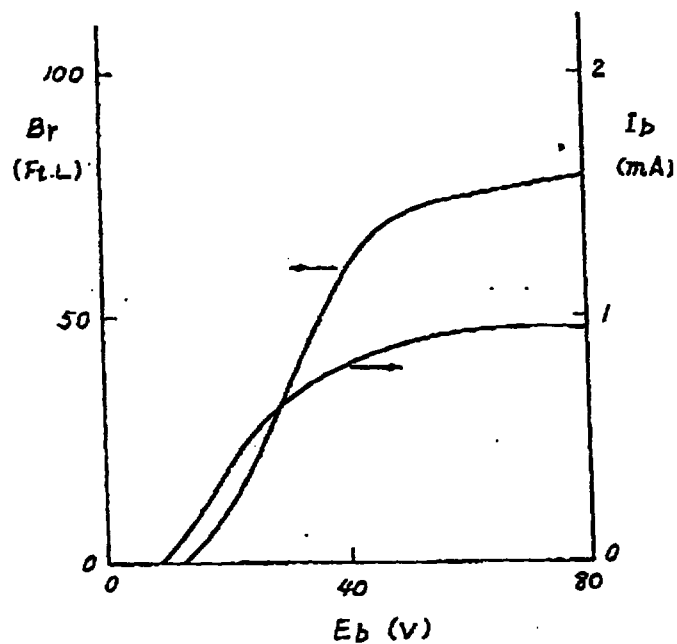
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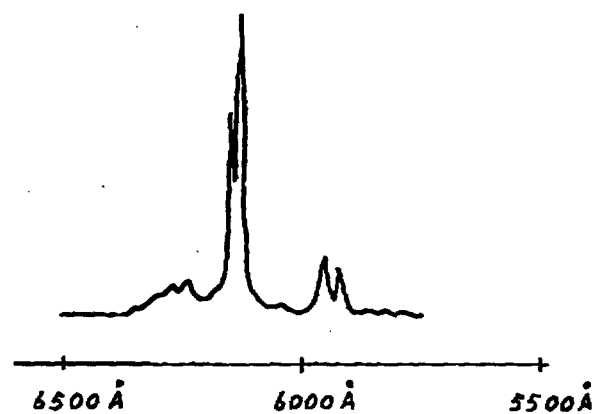
第1図



第2図



第3図



第4図

