

**MIXED GREEN-EMITTING PHOSPHOR
AND A CATHODE RAY TUBE ADOPTING THE SAME**

Background of the Invention

The present invention relates to a mixed green-emitting phosphor and a cathode ray tube (CRT) adopting the same, and more particularly, to a mixed green-emitting phosphor for enhancing afterglow characteristic and diminishing flicker and a CRT adopting the same.

In recent times, the prevalence of CRT display devices has been rapidly increasing and such devices have a close relation with our daily life. In many cases, this widespread usage is adversely affecting human eyes, and particularly, operators may suffer VDT (video display terminal) syndrome which is a sort of occupational disease caused by the extensive viewing of the display of a cathode ray tube. VDT syndrome is an impaired functioning of the eyes, which is caused by flicker, electromagnetic waves, and other properties of a CRT.

Accordingly, a great deal of research has gone into diminishing flicker as a way for preventing VDT syndrome. The result of the research shows that the flicker is affected by such factors as display size, scanning mode, afterglow and phosphor luminance. Therefore, methods for diminishing flicker through control of these factors can be used.

Among the methods to prevent flicker, much research has concentrated on controlling the refresh rate and enhancing the

afterglow characteristic. The present application relates to a method for improving the afterglow characteristic of the phosphor.

As components of the conventional phosphor of a color cathode ray tube, yttrium oxy-sulfide activated with europium ($\text{Y}_2\text{O}_2\text{S}:\text{Eu}$) as a red-emitting phosphor, zinc sulfide activated with copper and gold and co-activated with aluminum ($\text{ZnS}:\text{Cu},\text{Au},\text{Al}$), zinc sulfide activated with copper and co-activated with aluminum ($\text{ZnS}:\text{Cu},\text{Al}$) as a mixed green-emitting phosphor, and zinc sulfide activated with silver and co-activated with chlorine ($\text{ZnS}:\text{Ag},\text{Cl}$) as a blue-emitting phosphor have come into wide use. However, these phosphors are components having a short afterglow characteristic which gives rise to flicker. Accordingly, the need for a phosphor having good afterglow characteristic has been increasing.

Particularly, among red, green and blue-emitting phosphors, a great deal of research was concentrated on obtaining green-emitting phosphor having a long afterglow characteristic. Because green-emitting phosphor exerts influence above 60% on luminance of screen and thus it is easy to improve afterglow characteristic all over the screen by improving afterglow characteristic thereof.

$\text{ZnS}:\text{Cu},\text{Au},\text{Al}$ and $\text{ZnS}:\text{Cu},\text{Al}$ have come into use as a conventional mixed green-emitting phosphor, but both have a short afterglow characteristic; that is, a decay time of about 0.45ms. To the contrary, indium borate activated with terbium ($\text{InBO}_3:\text{Tb}$) and zinc silicate activated with manganese ($\text{Zn}_2\text{SiO}_4:\text{Mn}$) are known as phosphors having long afterglow and

good color purity. However, these phosphors are costly, exhibit poor luminance, and since an "afterimage" is caused owing to an overly long afterglow time, their practical use is somewhat restricted.

5 Summary of the Invention

The object of the present invention is to provide a mixed green-emitting phosphor having good afterglow characteristic for diminishing flicker.

10 It is another object of the present invention to provide a cathode ray tube adopting the mixed green-emitting phosphor of the present invention, for diminishing flicker and thus reducing eye-fatigue.

To accomplish the above object, there is provided according to the present invention, a mixed green-emitting phosphor comprising $\text{InBO}_3\text{:Tb}$ and one selected from ZnS:Cu,Au,Al and ZnS:Cu,Al .

To accomplish the above another object, there is provided according to the present invention, a cathode ray tube adopting the mixed green-emitting phosphors comprising $\text{InBO}_3\text{:Tb}$ and one selected from ZnS:Cu,Au,Al and ZnS:Cu,Al .

Preferably, the mixed green-emitting phosphor further comprises $\text{Zn}_2\text{SiO}_4\text{:Mn}$.

Particularly, the amount of each mixed green-emitting phosphor according to the present invention is preferred to be 40~90wt% of $\text{InBO}_3\text{:Tb}$, with the balance being ZnS:Cu,Au,Al or ZnS:Cu,Al . In the case of further comprising $\text{Zn}_2\text{SiO}_4\text{:Mn}$, the amount of each mixed green-emitting phosphor is preferred to

be 40~80wt% of $\text{InBO}_3\text{:Tb}$ and 10~30wt% of $\text{Zn}_2\text{SiO}_4\text{:Mn}$, with the balance being $\text{ZnS:C}\text{u,Au,Al}$ or $\text{ZnS:C}\text{u,Al}$.

Detailed Description of the Invention

5 A mixed green-emitting phosphor of the present invention is manufactured by mixing $\text{ZnS:C}\text{u,Au,Al}$ or $\text{ZnS:C}\text{u,Al}$ having high luminance and $\text{InBO}_3\text{:Tb}$ having a very long afterglow time and rather good color purity so as to improve the afterglow characteristic. The mixed green-emitting phosphor according to the present invention may also contain $\text{Zn}_2\text{SiO}_4\text{:Mn}$ which
10 exhibits excellent color purity and long afterglow time.

While the $\text{InBO}_3\text{:Tb}$ is difficult to put to practical use due to poor luminance thereof, it has a rather good color purity characteristic ($X=0.330$, $Y=0.592$), a long afterglow time, and excellent luminosity. While $\text{Zn}_2\text{SiO}_4\text{:Mn}$ has luminance
15 poorer than $\text{InBO}_3\text{:Tb}$, the $\text{Zn}_2\text{SiO}_4\text{:Mn}$ has a very long afterglow time and X-Y chromaticity coordinates (0.210, 0.700) nearly adjacent to coordinates (0.210, 0.710) initially determined by the National Television System Committee; that is, nearly ideal color purity.

20 In view of the aforementioned characteristics, a mixed green-emitting phosphor manufactured by suitably mixing $\text{InBO}_3\text{:Tb}$ with one selected from $\text{ZnS:C}\text{u,Au,Al}$ and $\text{ZnS:C}\text{u,Al}$ maintains luminance and color purity within a level suitable to practical use. Also, the mixed green-emitting phosphor not
25 only improves luminosity characteristics, but also can lengthen afterglow time to diminish flicker, compared with only one green-emitting phosphor selected from $\text{ZnS:C}\text{u,Au,Al}$

and ZnS:Cu,Al without InBO₃:Tb. Additionally, the green-emitting phosphor of the present invention can also contain Zn₂SiO₄:Mn which exhibits excellent color purity and long afterglow time.

5 Particularly, the mixing ratio of each phosphor is preferred to be 40~90wt% of InBO₃:Tb, with the balance being ZnS:Cu,Au,Al or ZnS:Cu,Al. In case of further comprising Zn₂SiO₄:Mn, 40~80wt% of InBO₃:Tb and 10~30wt% of Zn₂SiO₄:Mn, with the balance being ZnS:Cu,Au,Al or ZnS:Cu,Al, based upon
10 the total weight of the mixed green-emitting phosphor. Here, if the amount of InBO₃:Tb or Zn₂SiO₄:Mn is less than the determined range, the afterglow characteristic-enhancing effect is slight, and if more than the determined range, the adverse effect to luminance characteristic is predominant,
15 thereby impeding its practical use.

Each phosphor used to manufacture the mixed green-emitting phosphor of the present invention is prepared as follows:

1) Preparation of ZnS:Cu,Au,Al

20 0.048g of copper sulfate (CuSO₄·5H₂O) as an activator Cu component, 0.212g of chloroauric acid (HAuCl₄·4H₂O) as an activator Au component, 0.2g of aluminum fluoride (AlF₃) as a co-activator Al component, and 0.6g of ammonium iodide (NH₄I) as a flux were added to pure water. The thus-obtained solution
25 was added to 100g of ZnS and homogeneously mixed. Thereafter, the mixture was fired at 1000°C for two hours in a thermostable container under a reducing atmosphere with sulphur, followed by washing and drying, to obtain the

ZnS:Cu,Au,Al.

2) Preparation of ZnS:Cu,Al

The above-mentioned ZnS:Cu,Al was prepared in the same manner as described in the above 1) for the ZnS:Cu,Au,Al but without adding chloroauric acid ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$) as an activator Au component.

3) Preparation of $\text{InBO}_3\text{:Tb}$

3.3g of indium oxide (In_2O_3) and 1.5g of boric acid (H_3BO_3) as starting materials of InBO_3 , 0.121g of terbium oxide (Tb_2O_3) as an activator Tb component and lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) as a flux were homogeneously mixed and then fired at 1300° for three hours in a thermostable container, followed by washing and drying, to obtain the $\text{InBO}_3\text{:Tb}$.

4) Preparation of $\text{Zn}_2\text{SiO}_4\text{:Mn}$

4g of zinc oxide (ZnO), 6g of silicon dioxide (SiO_2) and 0.2g of manganese sulfate (MnSO_4) were homogeneously mixed and then fired at 1200°C for two hours, followed by washing and drying, to obtain the $\text{Zn}_2\text{SiO}_4\text{:Mn}$.

Hereinbelow, the present invention is described more concretely with reference to specific examples intended to illustrate the instant invention without limiting the scope thereof.

Example 1

The mixed green-emitting phosphor according to the present invention was prepared by mixing 30wt% of ZnS:Cu,Al and 70wt% of InBO_3 . A screen was manufactured using only the thus-obtained phosphor and then luminance of the screen was estimated.

The screen for color cathode ray tube was manufactured using the thus-obtained mixed green-emitting phosphor, $Y_2O_2S:Eu$ as a red-emitting phosphor and $ZnS:Ag,Cl$ as a blue-emitting phosphor. Then luminance, chromaticity coordinates, afterglow time and luminosity of the screen were estimated and the result described in the following Table 1.

As shown in Table 1, the phosphor layer of a cathode ray tube manufactured by using the mixed green-emitting phosphor of the present invention has rather good luminance as well as a color purity characteristic ($X=0.305$ and $Y=0.594$) near that of the European Broadcasting Union Standard ($X=0.290$, $Y=0.600$) which is widely followed as the new standard with respect to chromaticity coordinates. Therefore, the thus-manufactured phosphor layer can be put to practical use. Additionally, it has an afterglow time twenty times that of the phosphor layer using only $ZnS:Cu,Al$, to thereby diminish flicker drastically, and exhibits a good luminosity characteristic.

Examples 2-7

As shown in Table 1, the mixed green-emitting phosphor was prepared by varying the mixing ratio of each green-emitting phosphor within the range of the present invention. A screen was manufactured using only the thus-obtained phosphor and then luminance of the screen was estimated.

The screen for color cathode ray tube was manufactured using the thus-obtained mixed green-emitting phosphor, $Y_2O_2S:Eu$ as a red-emitting phosphor and $ZnS:Ag,Cl$ as a blue-emitting phosphor. Then luminance, chromaticity coordinates, afterglow time and luminosity of the screen were estimated and the

result is shown in the following Table 1.

As shown in Table 1, the above-obtained phosphor maintains luminance and color purity within a level suitable to practical use. Also, the above-obtained phosphor not only improves the luminosity characteristic, but also can lengthen the afterglow time to diminish flicker, compared with only one green-emitting phosphor selected from ZnS:Cu,Au,Al and ZnS:Cu,Al without $\text{InBO}_3\text{:Tb}$.

Comparative Examples 1-4

The screen for cathode ray tube was prepared in the same manner as described in Example 1 except that a single phosphor alone was used as a green-emitting phosphor component. And each characteristic was estimated and the result is shown in the following Table 1. As shown in Table 1, since one or more of the thus-estimated characteristics were extremely poor, its practical use is impeded.

Here, in the case of using ZnS:Cu,Al or ZnS:Cu,Au,Al alone, the screen exhibits good luminance but has a very short afterglow time (the major cause of flicker) and has a poor luminosity characteristic.

In the case of using InBO_3 or Zn_2SiO_4 alone, the luminosity characteristic is excellent. However, since the afterglow time is very long and luminance is not good, its practical use is impeded.

As mentioned above, the mixed green-emitting phosphor according to the present invention is manufactured by mixing $\text{InBO}_3\text{:Tb}$ with one selected from ZnS:Cu,Au,Al and ZnS:Cu,Al , optionally with $\text{Zn}_2\text{SiO}_4\text{:Mn}$ in the predetermined ratio.

Accordingly, the mixed green-emitting phosphor according to the present invention not only has good luminance and color purity but also enhanced afterglow and luminosity characteristics.

Table 1

Ex.	phosphor mixing ratio						luminance (%)		chromaticity coordinates		decay time (ms)	luminosity
	ZnS:Cu,Au,Al	ZnS:Cu,Al	InBO ₃ :Tb	Zn ₂ SiO ₄	A	B	X	Y				
1		30	70		82	93	0.305	0.594	9.4	good		
2		20	80		78	90	0.314	0.593	11	good		
3		30	40	30	77	92	0.281	0.606	10	good		
4		10	80	10	70	85	0.297	0.610	12	good		
5		50	50		93	97	0.290	0.601	3	normal		
6		40	60		87	95	0.299	0.598	4	normal		
7	40		10	50	82	90	0.265	0.623	4.2	normal		
comp. 1	100				100	100	0.299	0.587	0.45	poor		
comp. 2		100			105	101	0.270	0.610	0.45	poor		
comp. 3			100		63	75	0.330	0.592	32	excellent		
comp. 4				100	60	70	0.210	0.700	32	excellent		

* luminance

A: screen manufactured using green-emitting phosphor alone

B: screen manufactured using all phosphors

* conditions: 25kV, 500 μ A(green light), 25kV, 400 μ A(white light)

* tube: 14", 0.28 dot

* decay time: time to decay to 1/50th of initial luminance



What is claimed is:

1. A mixed green-emitting phosphor comprising $\text{InBO}_3\text{:Tb}$ and one selected from the group consisting of $\text{ZnS:C}\text{u,Au,Al}$ and $\text{ZnS:C}\text{u,Al}$.

5 2. A mixed green-emitting phosphor according to claim 1, wherein the amount of said $\text{InBO}_3\text{:Tb}$ is 40~90wt% based upon the total weight of said mixed green-emitting phosphor.

3. A mixed green-emitting phosphor according to claim 1, further comprising a $\text{Zn}_2\text{SiO}_4\text{:Mn}$.

10 4. A mixed green-emitting phosphor according to claim 3, wherein the amount of said $\text{InBO}_3\text{:Tb}$ and said Zn_2SiO_4 are 40~80wt% and 10~30wt%, respectively, based upon the total weight of said mixed green-emitting phosphor.

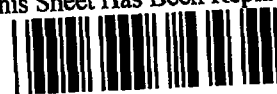
15 5. A cathode ray tube adopting a mixed green-emitting phosphor which comprises $\text{InBO}_3\text{:Tb}$ and one selected from the group consisting of $\text{ZnS:C}\text{u,Au,Al}$ and $\text{ZnS:C}\text{u,Al}$.

6. A cathode ray tube according to claim 5, wherein the amount of said $\text{InBO}_3\text{:Tb}$ is 40~90wt% based upon the total weight of said mixed green-emitting phosphor.

20 7. A cathode ray tube according to claim 5, wherein said mixed phosphor further comprises a $\text{Zn}_2\text{SiO}_4\text{:Mn}$.

25 8. A cathode ray tube according to claim 7, wherein the amount of said $\text{InBO}_3\text{:Tb}$ and said Zn_2SiO_4 are 40~80wt% and 10~30wt%, respectively, based upon the total weight of said mixed green-emitting phosphor.

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Abstract of the Invention

A mixed green-emitting phosphor is manufactured by mixing $\text{InBO}_3:\text{Tb}$ and one selected from $\text{ZnS}:\text{Cu}, \text{Au}, \text{Al}$ and $\text{ZnS}:\text{Cu}, \text{Al}$, optionally with $\text{Zn}_2\text{SiO}_4:\text{Mn}$. A cathode ray tube adopting the
5 mixed green-emitting phosphor not only has good luminance and color purity, but also enhanced afterglow and luminosity characteristics.

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28 MAR 1996

A MIXED GREEN-EMITTING PHOSPHOR AND A CATHODE RAY
TUBE ADOPTING THE SAME

A mixed green-emitting phosphor is manufactured by mixing $\text{InBO}_3\text{:Tb}$ and one selected from ZnS:C u,A u,A l and ZnS:C u,A l , optionally with $\text{Zn}_2\text{SiO}_4\text{:Mn}$. A cathode ray tube adopting the mixed green-emitting phosphor not only has good luminance and color purity, but also enhanced afterglow and luminosity characteristics.

17 MAR 1997

REVISED CLAIMS

What is claimed is:



1. A mixed green-emitting phosphor comprising:
 - (i) $\text{InBO}_3\text{:Tb}$;
 - (ii) A green-emitting phosphor selected from the group consisting of ZnS:Cu , Au , Al and ZnS:Cu, Al ; and
 - (iii) $\text{Zn}_2\text{SiO}_4\text{:Mn}$,

wherein the amounts of $\text{InBO}_3\text{:Tb}$ and Zn_2SiO_4 are 40-80 wt % and 10-30 wt % respectively, based upon the total weight of the mixed green-emitting phosphor.

2. A cathode ray tube adopting a mixed green-emitting phosphor, wherein the mixed green-emitting phosphor comprises:
 - (i) $\text{InBO}_3\text{:Tb}$;
 - (ii) A green-emitting phosphor selected from the group consisting of ZnS:Cu , Au , Al and ZnS:Cu, Al ; and
 - (iii) $\text{Zn}_2\text{SiO}_4\text{:Mn}$,

wherein the amounts of $\text{InBO}_3\text{:Tb}$ and Zn_2SiO_4 are 40-80 wt % and 10-30 wt % respectively, based upon the total weight of the mixed green-emitting phosphor.