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3,483,415

VANADATE FLUORESCENT MATERIAL

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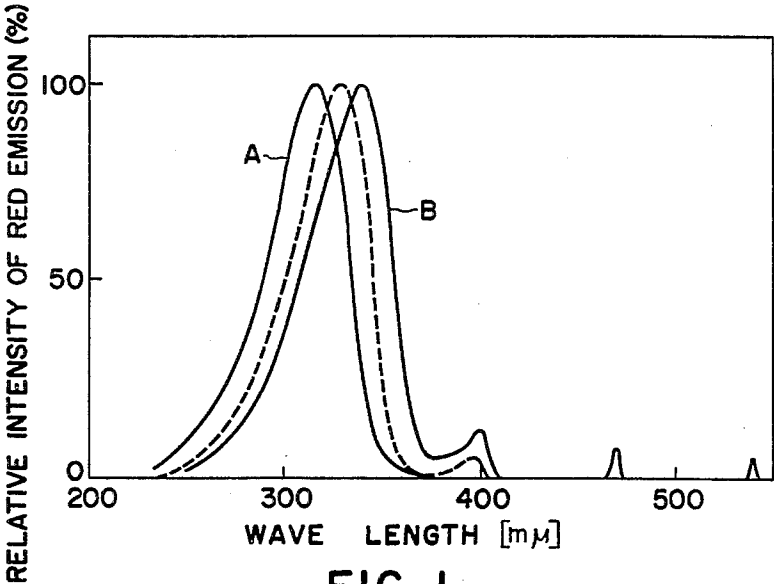


FIG. 1

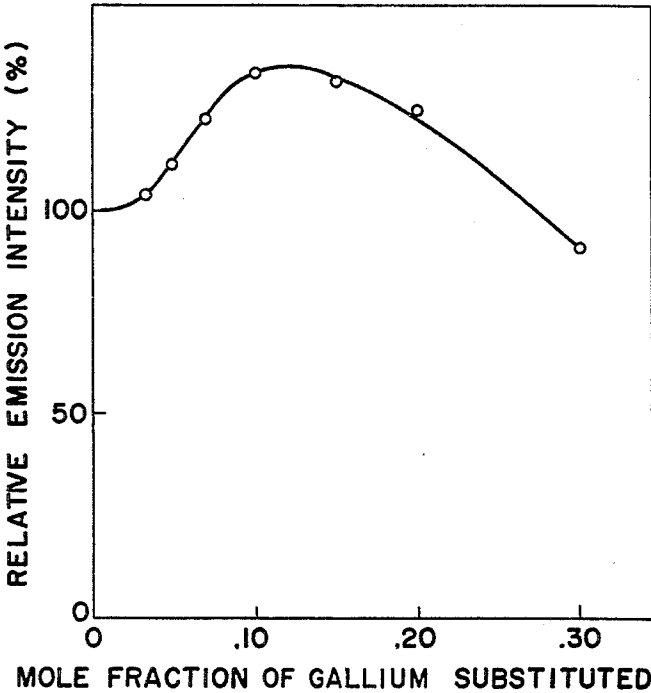


FIG. 2

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VANADATE FLUORESCENT MATERIAL

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6 Claims

ABSTRACT OF THE DISCLOSURE

A fluorescent material which is yttrium, gadolinium or lutetium vanadate activated by europium and containing 1 to 20 mol percent of gallium or thallium to enhance the luminescence of the vanadate, for use in mercury vapor fluorescent lamps and cathode ray tubes for color television.

This invention relates to a fluorescent material which emits visible light under the irradiation of invisible electromagnetic waves such as ultraviolet lights or X-rays or under the influence of energized material particles such as cathode rays, beta rays or alpha rays. In particular, the fluorescent material according to the present invention is one which emits red light under the irradiation of cathode rays or ultraviolet lights radiated from low- or high-pressure mercury lamps. More particularly, the fluorescent material according to the present invention is a fluorescent vanadate material activated with trivalent europium in rare earth elements.

An object of the present invention is to provide a fluorescent vanadate material which emits red light readily in response to cathode rays.

Another object of the present invention is to provide a fluorescent vanadate material which responds excellently to ultraviolet lights radiated from mercury discharge lamps to impart the color rendering property of fluorescent lamps.

Still another object of the present invention is to provide a fluorescent vanadate material which responds more readily to cathode rays or ultraviolet lights than does fluorescent yttrium vanadate material to emit red light with greater brightness.

A further object of the present invention is to provide a less expensive red-light emitting fluorescent material by substituting a part of the expensive yttrium, which is the component of the host crystal structure of yttrium vanadate fluorescent material by less expensive thallium.

Other objects of the present invention will become apparent from the following description.

As stated by L. G. Van Uitert, R. C. Linares, R. R. Soden and A. A. Ballman in the Feb. 1, 1962 issue of Journal of Chemical Physics, vol. 36, pp. 702-705, the fluorescent material of a europium-activated yttrium vanadate crystal is known to have a main emission band at 619 mμ attributable to the electron transition from the 5D₀ to the 7F₂ level of trivalent europium ions under the irradiation of ultraviolet lights. The main emission band at 619 mμ has a sub-band at 615 mμ. It has been disclosed by many workers that the energy levels in the vicinity of the ground energy level which is contributory to the luminescence in the trivalent europium ions are well shielded by 5d and 6s electron shells and are hardly influenced by the crystalline field of the host crystals into which the activator ions are introduced, unlike the changeable energy levels of activator ions other than rare earth elements contained in many fluorescent materials known hitherto. These levels are therefore not quite dissimilar to the free ion levels; they are affected little by the crystal-

line field and show merely linear expanses. For this reason, it is well known that the emission band widths caused by the electron transition between those levels in the trivalent europium ions introduced into the host crystals are almost linear.

The electron transition from the 5D₀ to the 7F₂ level which produces the main emission band at 619 mμ is attributed to an electric dipole transition, and whereas the electron transition is forbidden with free ions, it is allowed when trivalent europium ions are introduced in low symmetry crystals. When the electron transition from the 5D₀ to the 7F₂ level of trivalent europium ions is allowed, the emission band is not always fixed at 619 mμ as a result of the transition; but may vary over a wave length range of 610 to 620 mμ depending upon the structure of the host crystal. For example, when trivalent europium is introduced into an yttrium oxide crystal in a thallium oxide type crystal structure, the emission band is at 611.3 mμ. When trivalent europium is introduced into a tungstate crystal in a Scheelite structure, the main emission band is at 614 mμ. When trivalent europium is introduced into an yttrium vanadate crystal, the main emission band is at 619 mμ. The main emission bands given in these examples are invariably caused by electron transition from the 5D₀ to the 7F₂ level of the trivalent europium ions. However, the wave length positions of these main emission bands vary somewhat with the crystal structure, or more particularly with the symmetry of the ions which surround the trivalent europium ions introduced into the host crystal. In other words, they vary with the difference of the effect of the crystalline field upon the trivalent europium ions introduced into the crystal. The variation is attributed to the fact that the degeneracy of 7F₂ level of the trivalent europium ions is solved by the effect of the crystalline field of the crystal into which the trivalent europium ions are introduced, and the 7F₂ level is split into some levels and thus electron transitions take place from the 5D₀ level which has no such split levels toward the split levels. The most dominant effect of the crystalline field is due to the Stark effect. The probabilities of electron transitions between the 5D₀ level and the splitting levels of the 7F₂ level are not entirely the same for the 5D₀ level with respect to every splitting level of the 7F₂ level. The probability of electron transition from the 5D₀ level to the splitting level of the 7F₂ level which has the least Stark component is remarkably large as compared with that of the transition to the splitting level having a large Stark component. The Stark component of each splitting level of the 7F₂ level depends upon the structure of the host crystal into which the trivalent europium is introduced. Accordingly, the position of the main emission band is governed solely by the crystal structure into which the trivalent europium ions are introduced, as already stated, even if the electron transition occurs from the 5D₀ to the 7F₂ level of the trivalent europium ions.

The present invention will be described in more detail with reference to the accompanying drawings, in which:

FIGURE 1 shows a comparison between the excitation spectrum giving the emission at 619 mμ of the vanadate fluorescent material according to the present invention and that of the yttrium vanadate fluorescent material known hitherto. In FIG. 1, curve A is the excitation spectrum curve of yttrium-thallium vanadate fluorescent material and curve B is that of yttrium-gallium vanadate fluorescent material. The dotted line in FIG. 1 is the excitation spectrum curve of the yttrium vanadate fluorescent material known hitherto;

FIG. 2 shows the change in emission intensity at 619 mμ. of yttrium-gallium vanadate fluorescent material under the excitation of ultraviolet light at 365 mμ as a

function of the gallium content in the solid solution crystal.

According to the inventors' studies on yttrium, gadolinium and lutetium vanadate phosphors activated by europium, it has been found that the large and broad excitation band attributed to only the host crystal is moved by degrees, as shown in FIG. 1, either toward the short wave length side by thallium-substitution or toward the long wave length side by gallium-substitution depending upon the respective amount of substitution without however changing the structure of the crystal when a part of the yttrium, gadolinium or lutetium ions in the vanadate crystals of these ions is substituted by thallium or gallium ions. That is, in the crystal in which a part of rare earth ions is substituted by thallium or gallium ions, the substitution effects only the widely degenerated energy level of the host crystal without directly effecting the energy level in the inner electron shell of europium ion. The behavior of the effect depends only upon the amount of thallium of gallium ion substituted.

In general, in the case where the host crystal is a compound such as may form a solid solution without changing the structure of the crystal, e.g. in which cadmium sulfide or zinc selenide is mixed in zinc sulfide as a solid solution or in which calcium molybdate is mixed in cadmium molybdate a solid solution, it has been known experimentally that the movement of the position of the large excitation band attributed to the host crystal responds to the solid solution ratio in a correlative relationship. In these solid solutions, the solid solution ratio can be detected crystallographically because the ionic radii of both components forming the solid solution are somewhat different and the lattice constants vary according to Vegard's law.

In the fluorescent material according to the present invention, although it is difficult to determine crystallographically the solid solution ratio using a method such as X-ray diffraction analysis since the ionic radius of cation in the host crystal is closely similar to that of thallium or gallium substituted according to the present invention, it is nevertheless evident that a solid solution crystal, based on the fact that the excitation band attributed to the host crystal is continuously moved toward the short or long wave length side depending upon the amount of substituent.

Thus, the emission characteristics of the fluorescent material according to the present invention, in which the host crystal is one forming a solid solution and activated with trivalent europium, are almost similar to those of yttrium vanadate fluorescent material except for the change of the excitation band attributed to the host crystal in the vicinity of about 330 $m\mu$. As mentioned above, a host crystal could be formed which displays an emission at 619 $m\mu$ with a high efficiency, without changing the symmetry surrounding the trivalent europium. The movement of the main excitation band attributed to the host crystal, which determines the efficiency of the fluorescent material to use for fluorescent lamps, toward the longer or shorter wave length than 330 $m\mu$ provides a fluorescent material which respectively responds well to the main ultraviolet light of 365 $m\mu$ radiated from a high pressure mercury lamp, or responds well to the main ultraviolet light of 253.7 $m\mu$ of a low pressure mercury lamp, on the use of said fluorescent material to improve the color rendering of the lamps. That is, in excitation by the ultraviolet light of 365 $m\mu$ as shown in FIGURE 2, the emission intensity at 619 $m\mu$ is increased with the amount of gallium introduced in the yttrium vanadate fluorescent material. While the preferred amount of gallium introduced is within a wide range from 1 to 20 mol percent, the optimum amount thereof is about 10 mol percent. FIG 1, (Curve B) shows the excitation spectrum of yttrium-gallium vanadate fluorescent material which is formed at the optimum amount. The same results are also observed not only in the yttrium-gallium fluorescent mate-

rial but in the gadolinium-gallium vanadate or lutetium-gallium vanadate fluorescent material without a change of said optimum amount. Even when gallium is replaced by thallium in these fluorescent materials, only the source of excitation must be changed from ultraviolet light of 365 $m\mu$ to that of 253.7 $m\mu$ and there may be observed no essential difference. For the concentration of europium activator to obtain a fluorescent material having a high emission brightness in these solid solution fluorescent materials, the optimum concentration for each fluorescent material is within the range from 5 to 10 mol percent per mol of the host crystal while a fluorescent material having a good efficiency can be obtained over a wide range of concentration.

These fluorescent materials can be produced by mixing the oxide or a compound which is readily converted into the oxide by heating, of yttrium, gadolinium, lutetium, thallium, gallium and vanadium in a suitable combination and proportion thereof and heating the resulting mixture in air or other oxidizing atmosphere. In general, the addition of europium as the activator at the time of mixing the starting materials gives a rather good result, though, it may be added and heated in the form of the oxide or another europium compound which is easily converted into the oxide on heating, at the mixing of the starting salts of the host crystal or after the formation of the host crystal. An assistant agent or an oxidizing agent, for example, such as the halide salts of potassium or potassium perchlorate or periodate may be added in a suitable amount to the mixture on heating in order to facilitate the preparation. The starting materials should be mixed sufficiently so that the mixture may be finely divided and dispersed as homogeneously as possible. To attain the purpose, it is preferably to use a ball mill or a roll mill and the like. The procedure may be performed in a wet system in which a suitable amount of pure water or an organic solvent or the like is added. In this case, the assistant agent to facilitate the crystallization may be added after the mixture is dried. The mixture is filled in a vessel which will not melt on heating at a high temperature, e.g. a quartz or alumina crucible and is then heated at a suitable temperature in air or an oxidizing atmosphere in an electric furnace to yield the fluorescent material. It is preferable to heat at a temperature within the range from 800° to 1,500° C. for from 0.5 hr. to 7 hrs. and the optimum heating condition is to heat at about 1,000° C. for about 3 hrs., while the preferred heating condition may vary depending upon the element to be used, the kind of starting salt and the amount thereof used. The heating may be repeated several times. The grinding process using a ball mill etc., may be performed in the intervals of said repeated heating process; the insertion of said grinding process can provide a finely divided fluorescent material also having homogeneous particle size.

The fluorescent material according to the present invention emits brightly not only under excitation by ultraviolet lights but under the irradiation of particle rays such as cathode rays as well as under the irradiation of high energy radiation such as X-rays. Accordingly, the fluorescent material can be used in industry as a fluorescent material for the color-rendering of a high or low pressure mercury discharge lamp or a fluorescent material of red color component to be coated on an image receiving tube of color television or a fluorescent material for the detection of high energy radiation, in place of the fluorescent materials which have been used hitherto for such applications. That is, the fluorescent material according to the present invention is not only excellent in color-rendering for a discharge lamp, in color reproduction for color television and in visualization for the detection of radiation, but can also eliminate difficulties through which these characteristics can be displayed in industry due to the prior use of expensive rare earth elements in such kinds of fluorescent materials.

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This invention will now be described in more detail by the following examples.

EXAMPLE 1

	Mols
Yttrium oxide (Y_2O_3)	0.90
Thallium oxide (Tl_2O_3)	0.10
Vanadium pentoxide (V_2O_5)	1.00
Europium oxide (Eu_2O_3)	0.05

Said mixture is ground and mixed sufficiently by a ball mill, then filled in a quartz crucible and heated at 1,050° C. for 3 hrs. in air in an electric furnace to yield a red-emitting fluorescent material which have a main emission at 619 $m\mu$ under the excitation of ultraviolet lights, high energy radiations or cathode rays.

EXAMPLE 2

	Mols
Yttrium oxalate $Y_2(C_2O_4)_3$	0.80
Europium oxalate $Eu_2(C_2O_4)_3$	0.03

Said mixture is ground and mixed sufficiently by a ball mill, then filled in an alumina crucible and heated at 1,300° C. for 2 hrs. in air in an electric furnace to yield an yttrium-europium oxide fluorescent material. To the resulting fluorescent material,

	Mols
Gallium oxide Ga_2O_3	0.20
Ammonium vanadate NH_4VO_3	2.00

are further added and the mixture is mixed again in a ball mill. The resulting mixture is filled in a quartz crucible and heated at 1,100° C. for 3 hrs. in air in an electric furnace to yield a red-emitting fluorescent material which has a main emission of 619 $m\mu$ under the irradiation of ultraviolet lights, high energy radiations or cathode rays.

EXAMPLE 3

	Mols
Gadolinium oxide Gd_2O_3	0.85
Gallium oxide Ga_2O_3	0.15
Vanadium pentoxide (V_2O_5)	1.00
Europium oxide Eu_2O_3	0.05
Potassium chloride KCl	0.05

Said mixture is ground and mixed sufficiently by a ball mill, then filled in a quartz crucible and heated at 1,000° C. for 2 hrs. in air in an electric furnace to yield a red-emitting fluorescent material which have a main emission at 619 $m\mu$ under the excitation of ultraviolet lights, high energy radiations or cathode rays.

EXAMPLE 4

	Mols
Gadolinium oxalate $Gd_2(C_2O_4)_3$	0.95
Europium oxalate $Eu_2(C_2O_4)_3$	0.07

Said mixture is ground and mixed sufficiently by a ball mill, then filled in an alumina crucible and heated at 1,300° C. for 3 hrs. in air in an electric furnace to yield a gadolinium-europium oxide fluorescent material. To the resulting fluorescent material,

	Mols
Thallium sulfate ($Tl_2(SO_4)_3$)	0.05
Ammonium vanadate (NH_4VO_3)	2.00
Potassium periodate (KIO_4)	0.05

are further added and the mixture is again mixed by a ball mill. The resulting mixture is filled in a quartz cruci-

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ble and heated at 1,000° C. for 2 hrs. in air in an electric furnace to yield a red-emitting fluorescent material having an emission spectrum consisting of emitting rays which have a main emission at 619 $m\mu$ under the irradiation of ultraviolet lights, high energy radiations or cathode rays.

EXAMPLE 5

	Mols
Lutetium oxalate ($Lu_2C_2O_4$) ₃	0.90
Europium oxalate ($Eu_2(C_2O_4)_3$)	0.04
Thallium sulfate ($Tl_2(SO_4)_3$)	0.10
Ammonium vanadate (NH_4VO_3)	2.00
Potassium perchlorate ($KClO_4$)	0.10

Said mixture is ground and mixed sufficiently by a ball mill, then filled in a quartz crucible and heated at 950° C. for 5 hrs. in air in an electric furnace to yield a red-emitting fluorescent material which has a main emission at 619 $m\mu$ under the excitation by ultraviolet lights, high energy radiations or cathode rays.

EXAMPLE 6

	Mols
Lutetium oxide (Lu_2O_3)	0.80
Gallium oxide (Ga_2O_3)	0.20
Vanadium pentoxide (V_2O_5)	1.00
Europium oxide (Eu_2O_3)	0.06

Said mixture is ground and mixed sufficiently by a ball mill, then filled in a quartz crucible and heated at 1,050° C. for 3 hrs. in air in an electric furnace to yield a red-emitting fluorescent material which has a main emission at 619 $m\mu$ under the excitation by ultraviolet lights, high energy radiations or cathode rays.

We claim:

1. A fluorescent material consisting essentially of a europium activated vanadate of yttrium, gadolinium or lutetium in which thallium or gallium, in an amount sufficient to enhance the luminescence of the vanadate, is substituted for a like amount of the yttrium, gadolinium or lutetium.

2. A fluorescent material as claimed in claim 1 wherein the amount is from 1 to 20 mol percent.

3. A fluorescent material as claimed in claim 2 wherein the amount is about 10 mol percent.

4. A fluorescent high pressure mercury lamp comprising the gallium-containing fluorescent material as claimed in claim 1.

5. A fluorescent low pressure mercury lamp comprising the thallium-containing fluorescent material as claimed in claim 1.

6. A fluorescent screen for a cathode ray tube for color television comprising the fluorescent material as claimed in claim 1.

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