

[54] RARE EARTH ACTIVATED LANTHANUM AND LUTETIUM OXY-CHALCOGENIDE PHOSPHORS

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Related U.S. Patent Documents

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U.S. Applications:

[63] Continuation-in-part of Ser. No. 442,518, Mar. 24, 1965, abandoned.

[51] Int. Cl.<sup>2</sup> ..... C09K 11/46
[52] U.S. Cl. .... 252/301.4 S
[58] Field of Search ..... 252/301.4 S

[56]

References Cited

U.S. PATENT DOCUMENTS

2,462,547 2/1949 Pitha et al. .... 252/301.4 S
2,979,467 4/1961 Keller ..... 252/301.4 S
3,250,722 5/1966 Borchardt ..... 252/301.4 R

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[57]

ABSTRACT

A family of cathodoluminescent phosphors which consist essentially of oxy-chalcogenides of lanthanum and/or lutetium containing, for each mol of phosphor, between 0.0002 and 0.2 mol of dysprosium, erbium, europium, holmium, neodymium, praseodymium, samarium, terbium, or thulium. Up to 15 mol percent of the lanthanum and lutetium may be replaced with yttrium or gadolinium. The phosphors may be prepared by reacting the constituent elements as compounds thereof at temperatures between 900 and 1300° C. for 0.2 to 5.0 hours and then cooling the reaction product.

12 Claims, No Drawings

## RARE EARTH ACTIVATED LANTHANUM AND LUTETIUM OXY-CHALCOGENIDE PHOSPHORS

Matter enclosed in heavy brackets [ ] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

### CROSS REFERENCES

This is a continuation-in-part of patent application Ser. No. 442,518, filed Mar. 24, 1965 now abandoned, by Perry N. Yocom.

### BACKGROUND OF THE INVENTION

This invention relates to a family of new cathodoluminescent phosphors and to a method for preparing the novel phosphors.

In U.S. Pat. No. 2,462,547, there is described a family of phosphors consisting essentially of lanthanum oxy-sulfide containing two activators for example, europium and samarium. The phosphors of this family are infrared-stimulable storage phosphors; that is, they are useful for emitting light upon excitation with ultraviolet light and also emit upon subsequent stimulation with infrared light. These phosphors may be prepared by heating a mixture of lanthanum sulfate with suitable proportions of activator compounds in a reducing gas at about 800° C.

An object of the invention is to provide new phosphors which are particularly useful for emitting light upon excitation with cathode rays.

Another object is to provide a method for preparing the novel phosphors.

### SUMMARY OF THE INVENTION

The new phosphors consist essentially of oxychalcogenides of at least one of lanthanum and/or lutetium containing, for each mol of the phosphor, between 0.0002 and 0.2 mol of a member of the group consisting of dysprosium, erbium, europium, holmium, neodymium, praseodymium, samarium, terbium, and thulium. Up to about 15 mol percent of the lanthanum and lutetium may be replaced with yttrium and/or gadolinium. The preferred phosphors may be described as luminescent materials whose empirical formula is substantially:



where:

M' is at least one member of the group consisting of La and Lu;

M'' is a member of the group consisting of Dy, Er, Eu, Ho, Nd, Pr, Sm, Tb, and Tm;

O is oxygen;

Ch is at least one member of the group consisting of S, Se, and Te; and

x is between 0.0002 and [0.02] 0.2.

Up to about 15 mol percent of the M' may be replaced with Y and/or Gd to produce substantially equivalent brightness. Greater amounts than about 15 mol percent result in phosphors of inferior brightness.

The novel phosphors may be prepared by any of a variety of processes which bring together the constituents M', M'', Ch, and O at temperatures between 900 and 1300° C. For example, a mixture of oxides of M' and M'' may be heated in an atmosphere containing com-

pounds of CH. Or, a mixture of chalcogenates of M' and M'' may be heated in a reducing atmosphere.

In the new phosphors, only one activator element is used for M'', whereas two activator elements are used for M' in the prior art. Doubly-activated phosphors have been examined under cathode ray excitation and have been found to be unsuitable in most applications in cathode ray tubes for at least two reasons. The presence of two activator elements produces a less saturated emission color making them of little commercial interest. Also, when two activators are present, one activator may have a quenching effect upon the emission lines of the other activator. This has the overall effect of reducing the visual brightness of the emission.

The new phosphors may be used in a wide variety of applications as cathodoluminescent or photoluminescent emitters. [Particularly] *Particular* phosphors may be especially suited for particular uses. For example, phosphors in which M'' is Eu or Sm, such as La<sub>1.90</sub>Eu<sub>0.10</sub>O<sub>2</sub>S and Lu<sub>1.90</sub>Sm<sub>0.02</sub>O<sub>2</sub>S, may be used as red-emitting target materials in cathode ray tubes. Phosphors in which M'' is Tb, such as La<sub>1.97</sub>Tb<sub>0.03</sub>O<sub>2</sub>S, may be used as green-emitting target materials in cathode ray tubes.

The color and brightness of emission of a particular phosphor is related to the selection of M'' and x. The color of emission is directly related with the favored radiative energy transitions of the particular M'' selected. Hence, each phosphor will have an emission color which is characteristic of the M'' present. The favored energy transitions for a particular M'' is influenced by the value of x. Thus, some energy transitions are enhanced and others suppressed when the value of x is changed. For example, when M'' is Eu, the visual emission color of phosphors with low values of x is yellow-white, and is deep red for phosphors with values of x above 0.05.

The selection of M' and Ch have only a minor effect on the color of emission of the phosphor. Thus, with the same selection of M'' and x, oxy-sulfides, oxy-sulfoselenides, oxy-selenides, oxy-seleno-tellurides, and oxy-tellurides of lanthanum, lutetium, or lanthanum and lutetium may be provided which have substantially the same characteristics, but which may differ somewhat in their emission characteristics.

The new phosphors are preferably synthesized by coprecipitating oxalates of M' and M'' from a solution of nitrates of M' and M'' with oxalic acid. The coprecipitated oxalates are then converted to a mixed oxide by heating in air at temperatures between 600 and 1300° C. for 0.2 to 4 hours. The mixed oxide is then heated in an atmosphere of H<sub>2</sub>Ch at temperatures between 900 and 1300° C. for 0.2 to 2 hours.

The new phosphors may also be synthesized by one or more of the following processes which are generally described for making oxy-sulfides. Oxy-selenides and oxy-tellurides may be made by modifying the process in a manner known in the art.

(1) Heating a mixture of oxalates of M' and M'' in an atmosphere of H<sub>2</sub>S at temperatures between 900 and 1300° C. for 0.2 to 5.0 hours.

(2) Heating a mixture of sulfates of M' and M'' in a reducing atmosphere, such as a hydrogen atmosphere, at temperatures between 900 and 1300° C. for 0.2 to 5.0 hours.

(3) Heating a mixture of oxides of M' and M'' in a sulfurizing atmosphere, such as a carbon disulfide atmo-

sphere, at temperatures between 900 and 1300° C. for 0.2 to 5.0 hours.

(4) Heating a mixture of sulfur and oxides, or oxalates, or sulfates of M' and M'' in a nitrogen or hydrogen atmosphere at temperatures between 900 and 1300° C. for 0.2 to 5.0 hours.

(5) Heating a mixture of sulfates of M' and M'' in a sulfurizing atmosphere, such as hydrogen sulfide or carbon disulfide at temperatures between 900 and 1300° C. for 0.2 to 5.0 hours.

(6) Heating a substantially stoichiometric mixture of oxides and sulfides of M' and M'' in a neutral or reducing atmosphere at temperatures between 900 and 1300° C. for about 0.2 to 5.0 hours.

(7) Heating a mixture of sulphur, sodium carbonate and oxides or oxalates of M' and M'' in a covered crucible, in air, at temperatures between 900 and 1300° C. for 0.2 to 5.0 hours.

(8) Heating a mixture of sodium thiosulfate and oxides or oxalates or sulfates of M' and M'' in a covered crucible, in air, at temperatures between 900 and 1300° C. for 0.2 to 5.0 hours.

#### DESCRIPTION OF THE PREFERRED EMBODIMENT

##### Example 1

Dissolve about 315 grams of lanthanum oxide and 10.56 grams of europium oxide in nitric acid and dilute with water to a volume of about 3500 ml. Add to this nitrate solution with constant stirring about 2300 cc. of a 10% solution of oxalic acid, whereby a coprecipitate of lanthanum and europium oxalates is formed. Filter off the coprecipitate, and then wash and dry the coprecipitate. Heat the dry coprecipitate in air at about 1250° C. for about 1 hour to convert the coprecipitate to a mixed oxide. Then, heat the mixed oxide in an atmosphere of flowing hydrogen sulfide at about 1100° C. for about 1 hour and then cool to room temperature.

The product is a powder having a light rouge colored body color. With minor variation ordinarily occurring in the process, the product may have a different body color. For example, the body color may be white, straw, yellow, tan, pink, peach, orange, gray, or red. All of these varieties of the product of Example 1 have the empirical formula  $\text{La}_{1.94}\text{Eu}_{0.06}\text{O}_2\text{S}$  as evidenced by chemical and X-ray analysis.

The product is both photoluminescent and cathodoluminescent with a red visual emission color. The product is a line emitter type of phosphor with a principal peak at about 6260 A. and with a strong minor peak at about 6175 A. The product may be used as a red-emitting component in kinescopes; for example, for color television.

##### Example 2

Follow the procedure described in Example 1, except start with about 315 grams of lanthanum oxide and 10.47 grams of samarium oxide. The product is a white powder (which may also vary in body color) having an approximate empirical formula  $\text{La}_{1.94}\text{Sm}_{0.06}\text{O}_2\text{S}$ .

The product is both photoluminescent and cathodoluminescent with a red visual emission color. The product is a line emitter type of phosphor with a principal peak at about 6075 A. and with strong minor peaks at about 6100 A. and 6580 A. The product may be used as a red-emitting component in kinescopes.

##### Example 3

Follow the procedure described in Example 1 except start with about 319 grams of lanthanum oxide and 6.60 grams of praseodymium oxide. The product is a white powder (which also may vary in body color), having the approximate empirical formula  $\text{La}_{1.96}\text{Pr}_{0.04}\text{O}_2\text{S}$ .

The product is both photoluminescent and cathodoluminescent with a green visual emission color. The product is a line emitting type of phosphor, with a principal peak at about 5100 A., and with strong minor peaks at about 6200 and 6300 A.

##### Example 4

Follow the procedure described in Example 1 except start with about 322 grams of lanthanum oxide and 3.66 grams of terbium oxide. The product is a white powder (which also may vary in body color) having the approximate empirical formula  $\text{La}_{1.08}\text{Tb}_{0.02}\text{O}_2\text{S}$ .

The product is both photoluminescent and cathodoluminescent with a green visual emission color. The product is a line emitter type of phosphor, with a principal peak at about 5460 A. and with strong minor peaks at 4180, 4400, 4700, 5870 and 6280 A. The product may be used as a green-emitting component in cathode ray tubes.

##### Example 5

Follow the procedure described in Example 1 except start with about 309 grams of lanthanum oxide and 16.8 grams of neodymium oxide. The product is a white powder (which may vary in body color) having the approximate empirical formula  $\text{La}_{1.90}\text{Nd}_{0.10}\text{O}_2\text{S}$ . The product is both cathodoluminescent and photoluminescent with a blue visual emission color. The product is a line emitter type of phosphor, with a principal peak at about 9000 A. and with a minor peak at about 10,600 A.

##### Example 6

Follow the procedure described in Example 1 except start with about 387 grams of lutetium oxide and 11.13 grams of terbium oxide. The product is a white powder having the approximate empirical formula



The product is both photoluminescent and cathodoluminescent with a deep blue visual emission color. The product is a line emitter type of phosphor, with a principal peak at about 4590 A. and minor peaks at 4780 and 4820 A.

##### Example 7

Follow the procedure described in Example 1 except start with about 292 grams lanthanum oxide, 10.5 grams of yttrium oxide and 21.1 grams europium oxide. The product is a white powder having the approximate empirical formula  $\text{La}_{1.78}\text{Y}_{0.10}\text{Eu}_{0.12}\text{O}_2\text{S}$ . The product is both photoluminescent and cathodoluminescent with a red visual emission color. The product is a line emitter type of phosphor with a principal peak at about 6260 A. and with a strong minor peak at about 6175 A.

I claim:

1. A phosphor consisting essentially of an oxy-chalcogenide of at least one member of the group consisting of lanthanum and lutetium wherein up to [25] 15 mol percent of said lanthanum and lutetium is replaced with yttrium or gadolinium, said phosphor containing, for

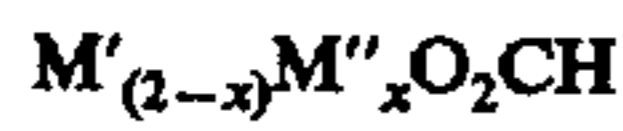
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each mol of said phosphor, between 0.0002 and 0.2 mol of a member of the group consisting of dysprosium, erbium, europium, holmium, neodymium, praseodymium, samarium, terbium, and thulium.

2. A phosphor according to claim 1 consisting essentially of a lanthanum oxy-sulfide containing between 0.0002 and 0.2 mol of europium per mol of said phosphor.

3. A phosphor according to claim 1 consisting essentially of a lutetium oxy-sulfide containing between 0.0002 and 0.2 mol europium per mol of said phosphor.

4. A luminescent material whose empirical formula is



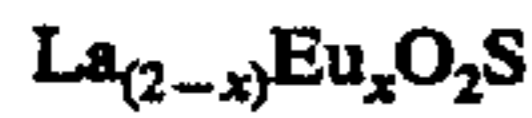
where: M' is at least one member of the group consisting of La and Lu, M'' is a member of the group consisting of Dy, Er, Eu, Ho, Nd, Pr, Sm, Tb, and Tm, O is oxygen, Ch is at least one member of the group consisting of S, Se, and Te, and x is between 0.0002 and 0.2.

5. A luminescent material according to claim 4 whose empirical formula is



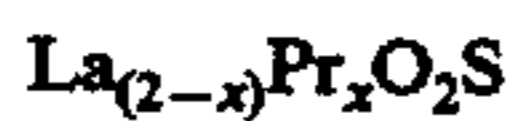
where: La is lanthanum, M'' is a member of the group consisting of Dy, Er, Eu, Ho, Nd, Pr, Sm, Tb, and Tm, O is oxygen, S is sulfur, and x is between 0.0002 and 0.2.

6. A luminescent material according to claim 5 having the empirical formula:



where x is between 0.0002 and 0.2.

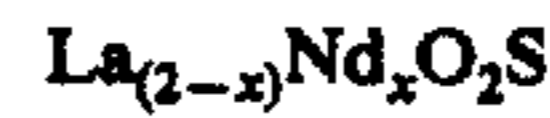
7. A luminescent material according to claim 5 having the empirical formula:



where x is between 0.0002 and 0.2.

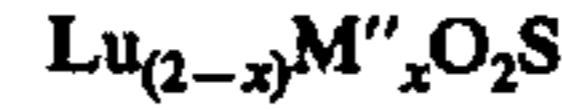
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8. A luminescent material according to claim 5 having the empirical formula:



5 where x is between 0.0002 and 0.2.

9. A luminescent material according to claim 4 whose empirical formula is



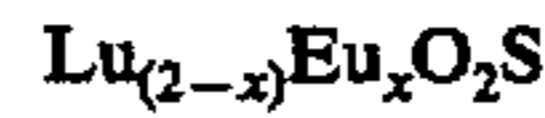
10 where: Lu is lutetium, M'' is at least one member of the group consisting of Dy, Er, Eu, Ho, Nd, Pr, Sm, Tb, and Tm, O is oxygen, S is sulfur, and x is between 0.0002 and 0.2.

15 10. A luminescent material according to claim 9 having the empirical formula:



20 where x is between 0.0002 and 0.2.

11. A luminescent material according to claim 9 having the empirical formula:



25 where x is between 0.0002 and 0.2.

12. In a method for preparing a phosphor whose empirical formula is



30 where: M' is at least one member of the group consisting of La and Lu and wherein up to about [25] 15 mol percent of the lanthanum and lutetium is replaced with yttrium and/or gadolinium; M'' is a member of the group consisting of Dy, Er, Eu, Ho, Nd, Pr, Sm, Tb and Tm; O is oxygen; Ch is at least one member of the group consisting of S, Se, and Te; and x is between 0.0002 and 0.2; the steps comprising reacting M, M'', Ch and O in the form of compounds thereof at temperatures between 900 and 1300° C. for 0.2 to 2.0 hours, thereby forming said phosphor, and then cooling said phosphor.

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