

RARE EARTH OXYSULPHIDE COMPOSITION,
A PROCESS FOR THE PREPARATION THEREOF,
AND USE THEREOF AS A LUMINOPHORE

The present invention concerns a rare earth oxysulphide composition, a process for the preparation thereof and use thereof as a luminophore.

It is known in the field of electronics that cathode ray tubes operate using a substantial level of energy of the order of 30,000V. Moreover there is a wish in that type of use to employ low-energy electrons, that is to say of the order of from 200 to 800V. This is especially the case with field emission displays (FED). This type of equipment comprises metallic microdots which emit low-energy electrons which subsequently excite a luminophorous material disposed on the display screen.

That luminophorous material must have two essential properties.

It must firstly have adequate optical characteristics, especially luminescence properties, and it must emit effectively in the desired colour.

It must secondly have electrical conductivity. The material must be capable of removing the charges when it is used in the above-mentioned application.

The problem lies in the difficulty of having a material which combines those two properties to an adequate degree. The luminous effectiveness of the material decreases with excitation potential. In addition there is a minimum excitation potential (V_{amin}) below which the material no longer presents conductivity. It is desired to use a potential range which is as low as possible, of the order of from 200 to 800V as indicated above. There is therefore a need for a material which has the lowest possible V_{amin} while retaining adequate luminous effectiveness.

The present invention seeks to provide a material which jointly presents adequate luminous effectiveness and conductivity in a voltage range corresponding to the required use (200 - 800V).





The present invention provides a composition comprising a rare earth oxysulphide and, as an additive, at least one rare earth element, said composition having at its surface an equilibrium or a deficit in respect of oxygen.

The invention also provides a process for the preparation of a rare earth oxysulphide composition which comprises calcining a composition comprising a rare earth oxysulphide and, an additive, at least one rare earth element, in the presence of hydrogen.

The invention also provides a luminescent composition which comprises a composition as defined above.

The products of the invention have a relatively low Vamin while retaining adequate luminous effectiveness for use as luminophores. They are particularly well suited to use for low-voltage luminescence situations, being a use in which they are subjected to low-energy electron radiation, that is to say of the order of from about at least 200V and at most about 800V.

In the accompanying drawings:

Figure 1 is an ESCA analysis spectrum of a product in accordance with the invention, and

Figure 2 is an ESCA analysis spectrum of a product in accordance with the prior art.

The product of the invention is a rare earth oxysulphide. The term rare earth is used here to denote elements of the group formed by yttrium and the elements in the periodic system with atomic numbers from 57 to 71 inclusive. The periodic system of elements to which reference is made is that published in the Supplement to the Bulletin de la Société Chimique de France No 1 (January 1966).

The rare earth oxysulphide may more particularly have the formula $\text{Ln}_2\text{O}_2\text{S}$ in which Ln denotes the rare earth.

The rare earth of the rare earth oxysulphide may, for example, be lanthanum, yttrium, gadolinium or lutetium.

In accordance with a particular embodiment of the invention the rare earth is gadolinium.

It will be noted that, irrespective of the presence of the additive which will be described hereinafter, the



product of the invention may comprise a plurality of rare earths which are involved in the composition of the oxysulphide itself.

The rare earth oxysulphide composition of the invention further comprises at least one rare earth element as an additive or doping substance. The purpose of the additive or doping substance is to give the oxysulphide a luminescence property. That rare earth is general different from that which forms the oxysulphide in the true sense. The rare earth will be selected depending on the emission colour which is desired for the luminophore. More particularly the additive or doping substance can, for example, be terbium, praseodymium, europium or samarium. Terbium and praseodymium will be more particularly selected for producing green luminophores. The additive will, for example, be europium or samarium for a red luminophore. It is entirely possible to use a plurality of additives in combination, such as for example terbium with praseodymium or europium with samarium.

Generally the additive is present in an amount of from 0.1 to 7%mol, and in particular from 0.1 to 4%mol, this amount being calculated in respect of the number of moles of additive/number of moles of additive + number of moles of rare earth oxysulphide $\text{Ln}_2\text{O}_2\text{S}$. The amount may be more particularly between 0.3 and 2%.

A main characteristic of the oxysulphide composition of the invention lies in its structure. It presents an equilibrium or a deficit in respect of oxygen at its surface. By way of non-limiting example and having regard on the other hand to the analysis procedures used, the term surface concerns here a thickness corresponding to about 5 atomic layers.

The terms equilibrium and deficit in respect of oxygen indicate the fact that, when the atomic ratio O:S at the surface of the oxysulphide is measured, that ratio is equal to or lower than the O:S stoichiometric ratio of the oxysulphide. For example, for an oxysulphide of the formula $\text{Ln}_2\text{O}_2\text{S}$, the stoichiometric ratio is 2:1. In the case of the product of the invention, that ratio is at most equal to 2:1. In the case of the known oxysulphides that ratio is higher



than 2:1 as a result, in particular, of an oxidation effect.

In accordance with a preferred embodiment of the invention the ratio O:S is markedly lower than 2:1 and may be equal to 0:1.

The surface state of the product of the invention as described hereinbefore can be revealed by ESCA analysis (Electro Spectroscopy for Chemical Analysis). This procedure permits chemical surface analysis. The presence of the peaks on the spectra reveals the nature of the elements at the surface of the product analyzed.

That surface state can also be revealed by measurement of the zeta potential of the product and determination of its isoelectric point. The products of the prior art, that is to say products which have not been subjected to the treatment of the invention, have a given pH for the isoelectric point while the products of the invention of identical composition but after treatment have a pH for the isoelectric point which is different and generally lower. By way of example the pH for the isoelectric point of a terbium-doped gadolinium oxysulphide is equal to 10 while the gadolinium oxysulphide of the same composition according to the invention has a lower pH for the isoelectric point.

Finally the product is preferably in the form of a powder. In that case the mean size of the particles of the powder is generally from 1 to 12 μm .

A process for the preparation of the composition of the invention will now be described.

This process essentially involves calcination of an oxysulphide in the presence of hydrogen.

The starting product is an oxysulphide which may be prepared by any means, for example by chamotting.

In accordance with a particular embodiment of the invention, instead of employing pure hydrogen, a hydrogen-bearing inert gas may be used. In that case the nature of the inert gas does not matter. Argon is usually employed.

The amount of hydrogen depends on the duration of the calcination operation and the amount of oxysulphide to be treated and the rate of deficit in respect of oxygen which is wanted for the product. When using a hydrogen-bearing inert gas, the amount of hydrogen generally varies from 1 to 20% by volume.



It is preferable to perform a sweep operation using hydrogen or a hydrogen-bearing inert gas, in the step of calcinating the oxysulphide.

The calcination temperature depends on the type of product calcined. However it is usually from 800 to 1200°C, preferably from 1000 to 1150°C. An excessively low temperature can be harmful to the optical properties of the product. An excessively high temperature can give rise to decomposition or sintering of the product.

The duration of the calcination operation also depends on the temperature and the quantity of oxysulphide to be treated and the rate of deficit in respect of oxygen which is wanted for the product. The calcination operation is usually effected for from 1 to 2 hours.

It is preferable to use a crucible of an inert metal such as platinum, which makes it possible to achieve a product affording better luminous effectiveness and in which the grains suffer less agglomeration.

The invention also concerns the luminescent compositions containing a rare earth oxysulphide of the type described above or of the type obtained by the process described above.

Those compositions and the oxysulphides of the invention can be used as a luminophore in low-voltage luminescence, in particular in the production of any apparatus suing such low-voltage luminescence, such as for example field emission display screens.

Finally the invention also concerns luminescent apparatuses, for example of the field emission display screen type, which incorporate the compositions or the oxysulphides as described above or as obtained by the process described above. In those apparatuses the oxysulphides are disposed on screens which are subjected to low-energy excitation. The use of the luminophores in the production of apparatuses involving low-voltage luminescence is effected in accordance with well-known procedures, for example by deposits on the screens by means of screen printing, sedimentation or electrophoresis.

The invention will now be further described in the following Examples.



In these Examples the zeta potential and determination of the isoelectric point are measured in the following manner. A concentrated solution is prepared, containing 2g of product in 130 ml of KNO_3 0.01 M. Agitation is effected for at least 24 hours and the solution is left to settle for at least 24 hours. A dilute suspension is then prepared by introducing into the supernatant material collected after settlement a few microlitres of product taken from the bottom substance. Three measurements in respect of mobility, pH and conductivity are taken and the mean of the histograms is calculated. Depending on the sign of said mean mobility, manual titration is effected, using KOH or HNO_3 , to look for the isoelectric point. A waiting time of 5 minutes is observed between the addition of acid or base and the mobility measurements. Three measurements are taken at each pH and the mean thereof is calculated.

The luminescence properties of the products in the Examples are measured by low-voltage cathodoluminescence of the products which are deposited without binder on a transparent substrate, under the conditions of excitation involving $1\mu\text{A}/\text{mm}^2$ in respect of direct current. The thickness of the layer of product on the substrate is $10\mu\text{m}$.

Example 1

The starting point taken is a gadolinium oxysulphide $\text{Gd}_2\text{O}_3\text{S}$ doped with terbium (1.5%mol).

It is calcined at different temperatures in a platinum crucible with a sweep of argon containing 10% hydrogen. A calcination period of 2 hours is used.

The calcined product emits a green luminescence. The results are set out in the following Table.

Calcination temperature °C	Luminous effectiveness at 400 V in lm/W	Vamin
1200	7	200V
1100	7	250V
900	5	250V

The pH of the isoelectric point of the product which



is calcined at 1200°C is 8.5.

By way of comparison the same product which is not calcined has a pH for the isoelectric point of 10 and does not have luminescence which can be measured in the range of from 200 to 800V.

Figures 1 and 2 show the differences between the product of the invention and the comparative product. These Figures are ESCA spectra. The axes of the abscissae indicate the bonding energies while the axes of the ordinates indicate a number of strokes. The peaks marked by 1 at about 1200 eV concern the electrons of the level 3d of the gadolinium and the peaks marked by 2 concern the electrons of the level 1s of oxygen. Comparison of the heights of the respective peaks 2 as between Figures 1 and 2 clearly shows a variation in the relative proportions between oxygen and gadolinium and more particularly, in the context of Figure 1, a deficit in respect of oxygen.

Example 2

This example uses an yttrium oxysulphide Y_2O_3S which is doped with europium (3%mol).

It is calcined at 1200°C in a platinum crucible with a sweep of argon containing 10% hydrogen. A calcination period of 2 hours is used.

The product emits a red luminescence. It has a luminous effectiveness at 400V of 2.5 Lm/W and a Vamin of 250V. The uncalcined product has a Vamin of 400V and a luminous effectiveness at 400V of 0.8 Lm/W.



CLAIMS

1. A composition comprising a rare earth oxysulphide and, as an additive, at least one rare earth element, said composition having at its surface an equilibrium in respect of oxygen.
2. A composition comprising a rare earth oxysulphide and, as an additive, at least one rare earth element, said composition having at its surface a deficit in respect of oxygen.
3. A composition according to claim 1 or claim 2 wherein the rare earth of the rare earth oxysulphide is lanthanum, yttrium, gadolinium or lutetium.
4. A composition according to any one of the preceding claims wherein the additive is terbium, praseodymium, europium and samarium.
5. A composition according to any one of the preceding claims wherein the additive is present in an amount of from 0.1 to 7%mol calculated in respect of the number of moles of additive/number of moles of additive + number of moles of rare earth oxysulphide.
6. A process for the preparation of a rare earth oxysulphide composition which comprises calcining a composition comprising a rare earth oxysulphide and, as an additive, at least one rare earth element, in the presence of hydrogen.
7. A process according to claim 6 wherein the calcination is effected in the presence of a hydrogen-bearing inert gas.
8. A process according to claim 7 wherein the hydrogen-bearing inert gas has a hydrogen content of from 1 to 20% by volume.
9. A process according to any one of the claims 6 to 8 wherein the calcination operation is performed by effecting a sweep of hydrogen or a hydrogen-bearing inert gas over the rare earth oxysulphide.
10. A process according to any one of claims 6 to 9 wherein the rare earth oxysulphide composition produced is as



defined in any one of claims 3 to 5.

11. A luminescent composition which comprises a composition as defined in any one of claims 1 to 5 or a composition prepared by a process as defined in any one of claims 6 to 10.

12. Use as a luminophore in low-voltage luminescence of a composition as defined in any one of claims 1 to 5 or which is prepared by a process as defined in any one of claims 6 to 10 or a composition as defined in claim 11.

13. Apparatus using low-voltage luminescence which comprises a composition as defined in any one of claims 1 to 5, a composition prepared by a process as defined in any one of claims 6 to 10, or a composition as defined in claim 11.

14. Apparatus according to claim 13 which is a field emission display screen.