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" Improvements in or relating to the preparation of green photo luminiscent copper activated zinc sulphide phospher (zns : cu)

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
Rafi Marg, New Delhi- 1, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860)

The following specification describes the nature of this invention.
This is an invention by Chittari Venkata Suryanarayana, Scientist Mohammed Iftikar Ahmed Siddiqi, Scientist and Alice Kurian (Miss), Senior Scientific Assistant, Central Electrochemical Research Institute, Karaikudi , Tamil Nadu, India, all Indians.

PRICE: TWO RUPEES

This invention relates to improvements in or relating to photoluminescent copper activated zinc sulphide (zinc sulphide: copper) more particularly the green-emitting photoluminescent zinc sulphide, excitable by the ultraviolet radiation of wavelength 3650 Å of mercury.

Hitherto it has been the practice to make sulphide phosphors, including zinc sulphides, whether cathodoluminescent, electroluminescent, triboluminescent or photoluminescent and other types as using inert and special atmospheres including H_2S, HCl and others. Moreover, the more essential details such as composition and processing conditions of making such phosphors are not given either in the technical or patent literature, although, because of their very great importance, considerably vast literature does exist on the subject of cathodo-, electro- and photoluminescence and others which have very wide civil and defence applications ranging from oscilloscope and radar screens to electroluminescent panels and mercury lamps. All these phosphors are at present largely imported in our country.

The object of this invention is to obviate these disadvantages by firstly eliminating the need of inert and special atmospheres and secondly working out the fullest possible details of the process so as to make the know-how on the manufacture of these phosphors available indigenously.

To these ends, we have developed a method of making a photoluminescent zinc sulphide phosphor using ordinary air atmosphere and worked out the more essential details and our invention broadly consists in taking a raw material batch comprising of zinc sulphide, a copper compound such as copper chloride copper sulphate, copper acetate in the range of concentration 10^{-5} to 10^{-4} gm mole per mole of zinc sulphide, a flux such as sodium chloride or any halide of the alkali metals in the concentration range 2 - 5% and zinc sulphate

tuents intimately to a slurry with the addition of suitable quantity of distilled water until the mass becomes almost dry, drying again in an air oven at 120°C, transferring to a silica crucible, and heating to a temperature in the range of 800°C to 1300°C for a duration depending on the quantity of the material, to bring about the solid state reaction. After heating, the sample is taken out from the hot furnace, and, while the crucible is kept closed, quenched in a medium such as air. The thus treated mass on cooling to room temperature is ground, washed with dilute acetic acid solution followed by washing with distilled water, kept at about 120°C to complete dryness and finally ground to the required fineness, for example, upto 300 mesh.

The spectral energy distribution of luminescence emission of such a resulting phosphor on excitation by monochromatised 3650 Å radiation of mercury (obtained from HBO 200 high pressure mercury lamp of 250 watts using a SP 500 monochromator) as measured by a Beckman DU Spectrophotometer is in the visible green region of wavelengths from about 4200 Å to 5950 Å with a peak at about 5000 Å. The intensity of luminescence emission is comparable with similar imported samples. While strongly luminescent to 3650 Å of mercury the resulting ZnS:Cu phosphor is also weakly luminescent to 2537 Å of mercury.

In our vast experimentation, we have found that the raw material zinc sulphide must be very pure within very low tolerance limits of the specific deleterious metallic impurities. All the chemicals except zinc sulphide must be analytically pure.

Zinc sulphide used was of a very high grade of purity prepared by a process developed earlier in this Institute patented under Indian Patent N°. 126439. By suitably modifying the composition and processing, it is possible to make photoluminescent zinc sulphide (green) of long phosphorescence which makes it

suitable in certain applications like watch and clock dials, instrument dials etc.,

Having broadly described our invention, the following examples are given to illustrate the invention:

EXAMPLE I

A raw material batch comprising the following is taken:

Zinc sulphide	:	5 gms
Copper sulphate	:	20 mg
Sodium chloride	:	100 mg
Zinc sulphate	:	50 mg

A typical phosphor may be prepared as follows: Added 20 mg of copper sulphate to pure zinc sulphide, the copper compound being in the form of an aqueous solution of such a strength as to make a paste with zinc sulphide, along with sodium chloride and zinc sulphate solutions, dried the product by mixing in a mortar and then in an air oven at about 120°C until completely dry, ground and placed in a silica crucible covered with a lid, inside another larger crucible. The outer crucible was also covered with a lid and the crucibles with the sample was kept in a furnace heated to 1050°C for 15 minutes. The temperature of firing can be in the range of 900 - 1100°C and duration can be from 15 minutes to one hour. The heated sample was taken out of the hot furnace and quenched in air, keeping the crucibles still closed, to room temperature. Ground the heated mass in a mortar, washed with a 3% solution of acetic acid followed by washing with distilled water. Dried the filtered phosphor powder at 120°C in an air oven and ground to 300 mesh particle size in a grinding mill. The relative spectral energy distribution of luminescence as excited by 3650 Å is given in Fig. 1 Curve 1 shown in the accompanying drawings

EXAMPLE II

A raw materials batch consisted of the following.

Zinc sulphide	20 gms
Copper acetate	22 mg
Sodium chloride	400 mg
Zinc acetate	220 mg

Proceeded exactly as in example I. The product gave a spectral energy distribution similar to curve 1 in figureI.

EXAMPLE III

A typical long phosphorescent phospher was prepared as follows A raw material batch consisted of the following -

Zinc sulphide	20 gms
Copper chloride	32 mg
Zinc sulphate	200 mg
Sodium chloride	400 mg

Processed as in the manner of example I except that the temperature of heating was 1150°C and duration was 30 minutes. Any temperature between 1100 and 1300°C can be chosen and the duration can be from 30 minutes to one and a half hour. The spectral energy distribution of luminescence emission is given in figure I Curve 2. The sample shows good phosphorescence of green colour.

EXAMPLE IV

Started with the following composition of the raw materials,

Zinc sulphide	10 gms
Copper nitrate	20.5 mg
Sodium chloride	200 mg
Zinc chloride	500 mg

Prepared the phosphor as described in example III. The product was found to give a spectral energy distribution similar to the curve 2 in figure I.

The following are among the main advantages of the invention:

1 The invention makes available indigenously the know-how on making photoluminescent zinc sulphide : copper by a simple, elegant process, requring raw materials and equipment available indigenously.

2 The invention does not require any special heating atmosphere.

3 Suitable modification in the composition and processing gives a long phosphorescent product.

Dated this twenty first day of August 1975.

Signed: C. V. Anuyanarayana

M. I. A. Siddiqi

Designation: Scientist

SCIENTIST

Senior Scientific Assistant

Dated this 18th day of September, 1975

Asstt. Patents Officer.
Council of Scientific & Industrial Research

145019

THE PATENTS ACT. 1970

COMPLETE SPECIFICATION

(Section—10)

IMPROVEMENTS IN OR RELATING TO THE PREPARATION OF GREEN PHOTOLUMINESCENT COPPER ACTIVATED ZINC SULPHIDE PHOSPHOR (ZnS : Cu)

Council of Scientific and Industrial Research, Rafi Marg, New Delhi - 1, India, an Indian Registered body incorporated under the Registration of Societies Act (Act XXI of 1860)

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This is an invention by Chittari Venkata Suryanarayana, Scientist, Mohammed Iftikhar Ahmed Siddiqe, Scientist and Alice Kurian, Senior Scientific Assistant, Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India, all Indian citizens.

This invention relates to improvements in or relating to the preparation of copper activated zinc sulphide phospher which will emit green light when excited by ultraviolet radiation of wavelengths at and below 365mm and is useful in optical and optoelectronic industries.

Hitherto zinc sulphide phosphers have been prepared by heating a mixture of luminescent grade zinc sulphide with small quantities of activaters, co-activaters and fluxes in suitable proportions at high temperatures inside a furnace in inert atmospheres like N_2 gas or reducing atmospheres like H_2S. Sometimes, the mixture is heated in HCl gas or a mixture of HCl gas and N_2. The activaters are usually metallic impurities or cations and the luminescent spectrum depends on the metallic impurity ion. For example, when copper is used as activater, the resulting phospher gives a green luminescence, while with manganese, the zinc sulphide phospher luminesces in the orange region. The co-activater is used to maintain the charge neutrality in the crystal and to facilitate the dissolution of the activater ions in the zinc sulphide lattice. The fluxes lower the melting point of the solid mixture and facilitate the diffusion of activater ions.

Green light emitting zinc sulphide phospher is usually obtained by doping the luminescent grade zinc sulphide with copper and chlorine. This is done by heating a mixture of the zinc sulphide, a copper salt and an alkali halide, particularly sodium chloride, in N_2 atmosphere at about 1000 to 1200°C. The zinc sulphide is mixed intimately with the other two compounds in suitable proportions and placed in silica or quartz tubes or silica or quartz crucibles and introduced into the furnace maintained at the temperature required. The heated mass is taken out after the required time, cooled and ground to proper particle size.

The object of this invention is to obviate the need of inert and special atmosphere and secondly to work out the fullest possible details of the process so as to make the know-how on the manufacture of these phosphors available indigenously.

To these ends, we have developed a method of making a photoluminescent zinc sulphide phosphor using ordinary air atmosphere and worked out the more essential unavailable details. Our invention broadly consists in taking a raw material batch comprising zinc sulphide, a copper compound such as copper chloride, copper sulphate, copper acetate in the range of concentration 10^{-5} to 10^{-4} mole, per mole of zinc sulphide, a flux such as sodium chloride or any halide of the alkali metals in the concentration range 2 - 5% by weight and zinc sulphate or chloride in the concentration range 1 - 2% by weight, mixing the constituents intimately to a slurry with the addition of a suitable quantity of distilled water, and further mixing until the mass becomes almost dry, drying again in an air oven at 120°C, transferring to a silica crucible, and heating to a temperature in the range of 800°C to 1300°C for a duration depending on the quantity of the material, to bring about the solid state reaction. After heating, the sample is taken out from the hot furnace and, while the crucible is kept closed, quenched in a medium such as air. The thus treated mass on cooling to room temperature is ground, washed with dilute acetic acid solution followed by washing with distilled water, kept at about 120°C to complete dryness and finally ground to the required fineness, for example, down to 300 mesh.

The spectral energy distribution of luminescence emission of such a resulting phosphor on excitation by 365mm radiation of mercury (obtained from HBO 200 high pressure mercury lamp of 250 watts using a SP 500 monochromator) as measured by a Beckman DU Spectrophotometer is in the visible green region of wave-

lengths from about 420nm to 595nm with a peak at about 500nm. The intensity of luminescence emission is comparable with similar imported samples. While strongly luminescent to 365nm of mercury radiation, the resulting ZnS:Cu phospher is also weakly luminescent to 253.7nm of mercury.

In our vast experimentation, we have found that the raw material zinc sulphide must be very pure within very low tolerance limits of the specific deleterious metallic impurities. All the other chemicals must be analytically pure.

In our experiments we have used the luminescent grade zinc sulphide obtained from 'Derby luminescents' and also that prepared by a process patented under Indian Patent No. 126439. The processed products, that is, both the phosphors, exhibit similar luminescence characteristics.

By suitably modifying the composition and processing, it is possible to make photoluminescent zinc sulphide phospher emitting green light of long phosphorescence which makes it suitable for certain applications such as watch and clock dials, instrument dials etc.,

The present invention consists of a process for the preparation of copper activated zinc sulphide phospher emitting green light when excited by near ultraviolet radiation and comprises a solid state reaction of zinc sulphide and a copper compound such as chloride, nitrate, sulphate, acetate in presence of a flux such as alkali halides at high temperature in a furnace wherein no special atmosphere is required.

Having broadly described our invention, the following examples are given to illustrate the invention:

EXAMPLE I

A raw material batch comprising the following is taken:

Zinc sulphide	:	5 g
Copper sulphate	:	20 mg
Sodium chloride	:	100 mg
Zinc sulphate	:	50 mg

A typical phosphor may be prepared as follows: Added 20 mg of copper sulphate to pure zinc sulphide, the copper compound being in the form of an aqueous solution of such a strength as to make a paste with zinc sulphide, along with sodium chloride and zinc sulphate solutions, dried the product by mixing in a mortar and then in an air oven at about 120°C until completely dry, ground and placed in a silica crucible covered with a lid, inside another larger crucible. The outer crucible was also covered with a lid and the crucibles with the sample were kept in a furnace heated to 1050°C for 15 minutes. The heated sample was taken out of the hot furnace and quenched in air to room temperature keeping the crucibles still closed. Ground the heated mass in a mortar, washed with a 3% solution of acetic acid followed by washing with distilled water. Dried the filtered phosphor powder at 120°C in an air oven and ground to 300 mesh particle size in a grinding mill. The relative spectral energy distribution of luminescence as excited by 365nm is given in Fig. 1 curve I/ shown in the drawing accompanying the provisional specification

EXAMPLE II

A raw materials batch consisted of the following:

Zinc sulphide	:	20 g
Copper acetate	:	22 mg
Sodium chloride	:	400 mg
Zinc acetate	:	220 mg

Proceeded exactly as in example I. The product gave a spectral energy distribution similar to curve 1 in figure I.

EXAMPLE III

A typical long phosphorescent phosphor was prepared as follows: A raw material batch consisted of the following:

Zinc sulphide	:	20 g
Copper chloride	:	32 mg
Zinc sulphate	:	200 mg
Sodium chloride	:	400 mg

Processed as in the manner of example I except that the temperature of heating was 1150°C and duration was 30 minutes. The spectral energy distribution of luminescence emission is given in figure 1 curve II. The sample shows good phosphorescence with green colour.

EXAMPLE IV

Started with the following composition of the raw materials:

Zinc sulphide	:	10 g
Copper nitrate	:	20.5 mg
Sodium chloride	:	200 mg
Zinc chloride	:	500 mg

Prepared the phosphor as described in example III. The product was found to give a spectral energy distribution similar to the curve II in figure 1. The sample shows good phosphorescence with green colour.

The following are among the main advantages of the invention:

1 The invention makes available indigenously the know-how on making green photoluminescent zinc sulphide:copper (ZnS:Cu) by a simple, elegant process, requiring raw materials and equipment available indigenously.

2. The invention does not require any special heating atmosphere.

3. Suitable modification in the composition and processing gives a long phosphorescent product.

The present invention concerns the preparation of copper activated zinc sulphide phosphor which will emit green light when excited by near ultraviolet radiation. The process involves a solid state reaction of zinc sulphide and a copper compound in presence of fluxes such as alkali halides at high temperature. Hitherto the high temperature and the details of the component parts were not clear in literature. Further the solid state reaction was, hitherto, brought about in an atmosphere of inert gases. In the present invention, the proportions of component parts are clearly delineated and the inert atmosphere is dispensed with.

We Claim:

1. A process, for the preparation of copper activated zinc sulphide phosphor emitting green light when excited by near ultraviolet radiations, comprising reacting phosphor grade zinc sulphide and a copper compound in the presence of a flux like an alkali halide, characterised in that the reaction is carried out in a temperature range of 800 to 1300°C in the presence of ordinary air atmosphere followed by quenching the resultant reaction mass in air and grinding the same to desired particle size.

2. A process as claimed in claim 1, wherein the reaction is carried out at preferred temperature of 1050°C in a container like a silica crucible.

Dated this 21st day of October, 1976.

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PROVISIONAL.

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Nº OF SHEETS:-
SHEET Nº :- 1

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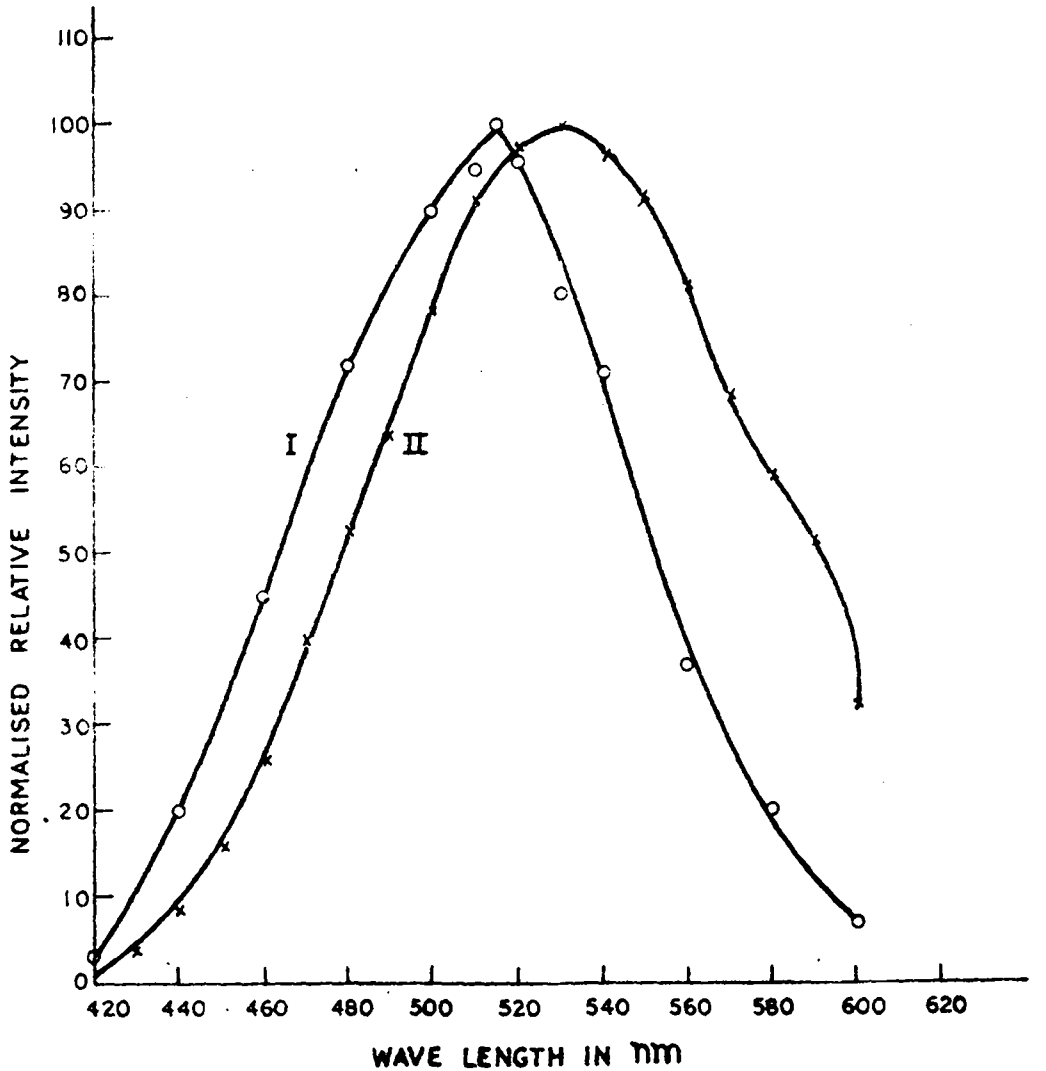

FIG. I

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