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" AN IMPROVED PROCESS FOR THE PREPARATION OF ZINC SULPHIDE : SILVER PHOSPHOR BLUE PHOTOLUMINESCENT MATERIALS. "

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH Rafi Marg, New Delhi-110001, 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 :-

PRICE : TWO RUPEES

This is an invention by Chittari Venkata Suryanarayana and Alice Kurian, Scientists of Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India, all Indians.

This invention relates to an improved process for the preparation of zinc sulphide-silver phosphor blue photoluminescent materials. These are highly useful in optoelectronic industries. The said phosphor is a polycrystalline powder of zinc sulphide containing silver as activator and emits a blue light when irradiated by ultraviolet radition of wave length 365 nm of the mercury line. This phosphor is particularly useful in coating the scintillating screens for use in radiation detectors to detect α- and β-particles, neutrons, X-rays and γ-rays.

In the prior art the blue light emitting photoluminescent phosphor of zinc sulphide activated with silver is known for its best scintillating properties and hence its use in scintillating screens used in radiation detectors and counters. Thus, the luminescent powder in suitable medium is coated on screens for use as scintilliating screens which is a component of the radiation detectors and counters manufactured in the electronic industry. Hence, the above said luminescent powder is useful in the electronic industry.

Hitherto zinc sulphide phosphors have been prepared by heating a mixture of luminescent grade zinc sulphide with small quantities of activators, co-activators and fluxes in suitable proportions at high temperature in inert atmospheres or special atmospheres like N_2, H_2S, HCl and the like.

Blue light emitting zinc sulphide phosphide phosphor is also conventionally prepared by doping the luminescent grade zinc sulphide with silver and chlorides. This is done by heating a mixture of zinc sulphide, a silver salt and an alkali halide particularly sodium chloride in N_2 atmosphere at about 800° to 1000°C. The zinc sulphide is mixed intimately with the other two compounds in suitable proportions and placed in silica or ceramic crucibles and introduced into the furnace at the temperature required. The heated mass is taken out after the required time, cooled and ground to the proper particle size and subsequently to the chemical treatment.

The main object of this invention is to eliminate the need of the special atmosphere and thus to save the expenditure on maintenance and control of the same.

The main advantages of the process of this invention are that: it gives out precisely a newly worked out procedure to get intense blue luminescence based on zinc sulphide raw material, special atmospheres which involve higher cost of production in the existing practice are totally avoided, the phosphor obtained by this method is very fine in comparison with the commercially available blue phosphor.

This has certain advantages is processing optoelectronic screens, one such being that of obtaining high resolutions in imaging. The importance becomes accentuated by the fact that grinding for further fineness of a zinc sulphide phosphor often reduced the luminescence output of the same. This is now

avoided.

The main principle underlying the invention is that the ingredients of the raw mix inside the crucibles, form in the furnace, an atmosphere of gases most favourable for the growth of the polycrystalline luminescent phosphor from the amorphour-like zinc sulphide powder.

The oxidisable sulphur containing compound used on heating decomposes and combines with the oxygen present in the furnace to form oxides of sulphur to provide an atmosphere.

Accordingly this invention provides an improved process for the preparation of zinc sulphide-silver blue photoluminescent phosphor comprises heating a mixture of zinc sulphide, a silver salt and an alkali halide a flux in an inert atmosphere at 800°-1000°C characterised in that the zinc sulphide admixture is placed in a ceramic crucible and heated to a temperature in the range of 800-1000°C thereafter heating the ceramic crucible in another bigger crucible containing an oxidisable sulphur compound and closed to provide an atmpsphere whih exclude oxygen.

According to a feature of the invention the phosphor forming admixture contains 5×10^{-5} to 5×10^{-4} mole of silver per mole of zinc sulphide, 2 to 10% by weight of the alkali chloride and 1-2% of the sulphur containing compound by weight of zinc sulphide.

According to a still another feature of the invention the sulphur containing compounds used are oxidisable sulphur

compounds like organic or alkali/alkaline earth metal compounds.

According to a still further feature of the invention the firing in a closed furnace is carried out at 800-1000°C.

We have thus developed a method of making a photoluminescent zinc sulphide phosphor without using any special atmosphere and worked out the more essential details and our invention broadly consists in taking a raw material batch comprising zinc sulphide, a silver compound in the form of its nitrate, sulphate or chloride, or any other water soluble silver compound in the range of concentration 5×10^{-5} to 5×10^{-4} mole of silver per mole of zinc sulphide, a halide flux preferably sodium chloride concentration range 2 to 15% and zinc sulphate in the concentration range of 1 to 5%, mixing the constituents intimately to a slurry with the addition of required quantity of distilled water and grinding it until the mass becomes dry. The dried mass is collected,washed and mixed with furthr quantity of double distilled water and making a slurry, mixing and stirring continuously to dryness, if necessary to speed up the experiment, at temperature a temperature around 60°C, drying again in an air oven at about 120° to 180°C transferring into a silica crucible, and heating at a temperature in the range of 800° to 1000°C for a duration depending on the quantity of the material and size of the particle to bring about the solid state reaction. The silica crucible is kept in another bigger crucible containing an oxidisable sulphur compound and closed to provide an atmosphere which excludes oxygen. After heating, the sample is cooled to room temperature in a time of

one to 2 & 1/2 hours, washed with water followed by dilute acetic acid and distilled water to remove oxide layer and excess flux. The filtered powder is dried to complete dryness and sieved. The advantage of this method is that the resultant phosphor is a fine powder. This phosphor powder gives an intense blue coloured light when irradiated by long wavelength ultraviolet light.

The spectral energy distribution of luminescence emission of thus prepared phosphor, on excitation by monochromatic radiation of wavelength 365 nm from a mercury lamp, as measured by a Beckmann DU Spectrophotometer is shown in the figure of the accompanying drawings in the visible blue region of wavelength from about 400 nm, to 540 nm with a peak around 460 nm. The intensity of blue emission is comparable to that of similar imported phosphor. While strongly photoluminescent to 365 nm line of mercury the resulting ZnS:Ag phosphor is moderately bright to 253 nm line of mercury also.

In our research and development investigation, we have found that the raw material-zinc sulphide must be very pure within very low tolerance limits of the specific deleterious metallic impurities like Fe, Co, Ni, Cu, Ag, Pb and the like., all the other chemicals need be only analytically pure.

Zinc sulphide used by us is of a high grade of purity and as prepared by a method described in our prior Indian Patent no. 126439.

As no special gas is used during heating in the furnace, the expenditure on gas and its maintenance is avoided.

The present invention concerns the preparation of silver activated zinc sulphide phosphor which will emit blue light when excited by near ultraviolet radiation. The process involves a solid state reaction of zinc sulphide powder and a silver compound in presence of fluxes such as alkali halides at high temperature. Hitherto the solid state reaction was brought about in a special gas atmosphere. In the present invention, the proportions of component parts are clearly delineated and the special atmosphere is dispensed with.

The essential steps of the process are:

a) Thorough mixing of the ingradients in suitable proportions and drying,

b) Drying to absolute dryness in an air oven at about 120° to 180°C.

c) Keeping the sulphur containing compound in the outer crucible,

d) Firing the dry powder of (c) in a furnace at around 900°C,

e) Cooling the heated product to atmospheric temperature in a time of 1 to 2 & 1/2 hours,

f) Washing the cooled product with water, acetic acid solution etc.

g) Drying the product in (f) to absolute dryness in an air even at about 160°C.

All the basic raw materials are available indigenously. The phosphor grade zinc sulphide is prepared from the indigenously

available raw material by the process of the Indian Patent No. 126439 developed by us. The process works well in the temperature range of the furnace between 800° and 1000°C. Optimum reaction condition is the temperature of firing being 900°C. The product of the process is the photoluminescent phosphor emitting blue light when excited by long wave ultraviolet light.

Having broadly described the invention, the following example is given to illustrate the invention:

Example

A raw material batch comprising the following composition is taken:

Zinc sulphide (ZnS)	..	5 g
Silver nitrate	..	1.0 mg
Sodium chloride	..	0.5 g
Zinc sulphide	..	50.0 mg

Added the silver nitrate to the zinc sulphide, the silver compound being in the form of an aqueous solution of such a strength as to make a paste with zinc sulphide along with the sodium chloride and zinc sulphate solutions, dried the product by mixing in a mortar with pestle and then adding further quantity of distilled water to the collection of the crushed raw-mix just to make a paste, mixing again in a mortar with pestle until dry and drying completely for several hours in an air oven at 160°C, ground and placed in a silica crucible having a capacity of 15 ml, covering it with its lid and finally placed about 0.5 g of an

oxidisable sulphur containing organic or alkali or alkaline earth metal compound or any sulphur compound which does not contain metallic ions other than Ag, Zinc, alkali metals, alkaline earth metals and such other harmless ones, inside the outer crucible so as to be in contact with the surrounding environment. The outer crucible was also covered with a lid and fired in a furnace at 900°C for 30 mits. The same was cooled to room temperature. Ground the heated mass in a mortar gently with pestle, washed with a 3% v/v solution of acetic acid followed by water. Dried the filtered phosphor powder in an air oven at 160°C for 10 to 16 hrs. The relative spectral energy distribution of luminescences as excited by the mercury line of wavelength 3650 A° is given in Figure 1.

WE CLAIM:

1. An improved process for the preparation of zinc sulphide-silver blue photoluminescent phosphor comprising heating a mixture of zinc sulphide, a silver salt and an alkali halide as flux in an inert atmosphere at 800°-1000°C characterised in that the zinc sulphide admixture is placed in a ceramic crucible and heated to a temperature in the range of 800-1000°C thereafter the ceramic crucible is heated in another bigger crucible containing an oxidisable sulphur compound and closed to provide and atmosphere which excludes oxygen.

2. An improved process as claimed in claim 1 wherein the phosphor forming admixture contains $5x10^{-5}$ to $5x10^{-4}$ mole of silver per mole of zinc sulphide, 2 to 10% by weight of the alkali chloride and 1-2% of the sulphur containing compound by weight of zinc

sulphide.

3. An improved process as claimed in claims 1 or 2 wherein silver compound used is a water soluble silver compound like its nitrate, sulphate or chloride and the alkali halide flux used is sodium chloride or an admixture of sodium chloride and zinc sulphate.

4. An improved process as claimed in any of the preceding claims wherein the sulpher containing compounds used are oxidizable sulphur compounds like organic or alkali/alkaline earth metal compounds.

5. An improved process as claimed in claim 4 wherein the heating in the ceramic crucible is carried out at a temperature of 900°-960°C for at least a period of 30 minutes.

6. An improved process for the preparation of zinc sulphide-silver blue phosphor photoluminescement material substantially as herein described and illustrated.

Dated this 9th day of July, 1984.

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COMPLETE SPECIFICATION

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Nº OF SHEETS :- 1

SHEET Nº :- 1

Pat. Appln. no. ~~557/25~~/64

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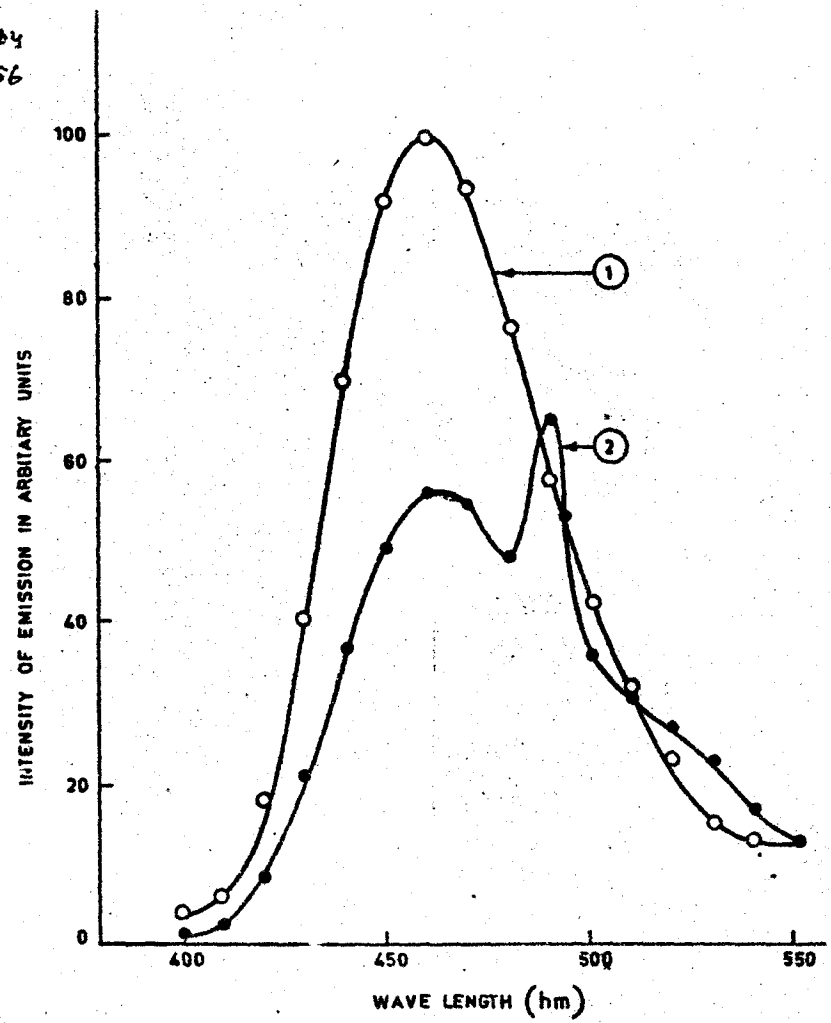

FIG-1

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