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PROVISIONAL SPECIFICATION.

IMPROVEMENTS IN OR RELATING TO THE PREPARATION OF PHOSPHOR GRADE ZINC SULPHIDE MATERIAL USEFUL FOR LUMINESCENT DEVICES.

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.

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This invention relates to improvements in or relating to preparation of phosphor grade zinc sulphide material useful for luminescent devices.

High purity zinc sulphide known as phosphor grade zinc sulphide has been the starting material for further treatment involving introduction of small quantities of metallic ions called dopants as a result of which the thus treated zinc sulphide could be used as a material for photo-luminescent, electroluminescent and cathodo-luminescent devices. The hitherto known method of preparing phosphor-grade zinc sulphide involved a high purity zinc salt as the starting material, passing of hydrogen sulphide gas scrupulously purified by passing through a train of traps to absorb unwanted impurities in hydrogen sulphide and collecting the precipitated zinc sulphide and drying for subsequent treatment to yield the desired luminescent material for the required purpose. The purification of hydrogen sulphide and the conditions of precipitation are rather critical and have so far been the main drawback for a successful preparation of the ultimate luminescent device. Further, even the method of obtaining phosphor grade zinc sulphide by the hydrogen sulphide method is covered in patents and the parameters involved are not explicit. Kramereva et al published in 1967 a paper wherein they indicated the preparation of zinc sulphide with thiourea in ammonia solution obtaining the final product in two steps : (1) by precipitation of a product containing 14-25% basic salt (2) by digestion for several hours with alkaline thiourea. This method is time consuming and involves two steps and is not less laborious than the method of preparation of zinc sulphide using hydrogen sulphide gas.

In this background the object of this invention is to work out an easy method of obtaining phosphor grade quality of zinc sulphide, which on subsequent sensitization by doping with the appropriate metal ion will give the required luminescence in the desired device.

To these ends the invention broadly consists in taking a mixture of a soluble inorganic or organic zinc salt and an organic sulphur compound like thiol, thiourea, substituted alkyl thioureas, thioacetamide or some inorganic thiocompounds like thiosulphate in aqueous solution at the laboratory temperature and then adjusting the pH to be on the alkaline side around 10-13 to get the desired precipitate of zinc sulphide by the addition of a strong alkali. Instead of a soluble zinc salt the starting material can be zinc oxide dissolved in strong alkali. The precipitation is near completion in about an hour and is hastened considerably to half the time by sufficient stirring. The zinc sulphide obtained by us is naturally photoluminescent due to self-activation.

The following typical examples are given to illustrate the invention :

EXAMPLE I

The method consists in preparing a 1 M solution of $ZnSO_4 \cdot 7H_2O$, adding an equal volume of 2 M Thiourea solution followed by a strong alkali (about 50% concn.) until the pH of the clear solution so obtained is near about 10.5 at the laboratory temperature. The solution is kept stirred using a magnetic stirrer for about one hour when almost theoretical amount of zinc sulphide is precipitated. Then the contents of the bath are diluted with water, washed by decantation and the precipitate of zinc sulphide is dried to 100°C in air oven. The luminescent grade zinc sulphide so obtained is doped with metal ions like Pb^{2+} , Ag^+ etc. by adding the dopant either to the precipitating bath or by the suspension of the zinc sulphide powder in a dilute solution of the dopant for the required period. The doped material so obtained is found to exhibit photoluminescence as reported in literature.

EXAMPLE II

Sufficient quantity of zinc oxide is dissolved in 100 cc of 2.5 to 5 N acetic acid followed by twice the weight of solid thiourea such that the clear solution so obtained must have a pH around 4.5. A strong alkali (30% solution) is added to the above solution until its pH reaches 13 and the solution is kept for 1 hour at room temperature. While zinc sulphide is precipitated which is filtered off after washing several times by decantation until free from alkali. The precipitate is dried at 100°C and the zinc sulphide powder so obtained is doped with metal ions like Pb^{2+} , Ag^+ etc. The doped material is found to exhibit the photoluminescence as reported in literature.

EXAMPLE III

A saturated solution of ZnO in strong alkali (approximately 40% concn.) is prepared. Its pH was near about 13. A saturated solution of thiourea, twice that of zincate solution by volume is added and the mixture is kept stirred for one hour using a magnetic stirrer. The precipitated zinc sulphide is filtered off, washed thoroughly with distilled water and dried. The phosphor grade zinc sulphide powder is activated with Pb^{2+} , Ag^+ etc. and the products are found to exhibit photoluminescence as reported in literature.

The following are among the main advantages of the the invention :

(i) Compared to the conventional method wherein H_2S is used, which in turn requires a series of purifying columns etc. this method is cheaper and straight.

(ii) Compared to the Russian method wherein thiourea is used, this method is simple and of only one stage and is performed at laboratory temperature.

(iii) The zinc sulphide we get by our process is naturally photo luminescent due to self-activating property of the same whereas there is no such report by hitherto known processes.

Price : TWO RUPEES.

(iv) In hitherto known methods addition of dopants required subsequent firing to get the characteristic photo-luminescence. But in our case dopants added to the bath gave ZnS which straightaway gave photoluminescence.

(v) On the whole our process is easy of manipulation

and saves time and straightaway gives phosphor grade zinc sulphide.

(R. BHASKAR PAI)

Patents Officer,

Council of Scientific and Industrial Research.

Dated this 24th day of April 1970.

COMPLETE SPECIFICATION

IMPROVEMENTS IN OR RELATING TO THE PREPARATION OF PHOSPHOR GRADE ZINC SULPHIDE MATERIAL USEFUL FOR LUMINESCENT DEVICES .

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAJI MARG, NEW DELHI-1, 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.

The invention relates to improvements in or relating to preparation of phosphor grade zinc sulphide useful for luminescent devices.

High purity zinc sulphide known as phosphor grade zinc sulphide has been the starting material for further treatment involving introduction of small quantities of metallic ions called dopants as a result of which the thus treated zinc sulphide could be used as a material for photo-luminescent, electroluminescent and cathodeluminescent devices. The hitherto known method of preparing phosphor grade zinc sulphide involved a high purity zinc salt as the starting material, passing of hydrogen sulphide gas scrupulously purified by passing through a train of traps to absorb unwanted impurities in hydrogen sulphide and collecting the precipitated zinc sulphide and drying for subsequent treatment to yield the desired luminescent material for the required purpose. The purification of hydrogen sulphide and the conditions of precipitation are rather critical and have so far been the main drawback for a successful preparation of the ultimate luminescent device. Further, even the parameters involved in obtaining phosphor grade zinc sulphide by the hydrogen sulphide method are not explicit. Kramereva *et al* published in 1967 a paper wherein they indicated the preparation of zinc sulphide with thiourea in ammonia solution obtaining the final product in two steps: (1) by precipitation of a product containing 14-25% basic salt (2) by digestion for several hours with alkaline thiourea. This method is time consuming and involves two steps and is not less laborious than the method of preparation of zinc sulphide using hydrogen sulphide gas.

The most important factor on which the further sensitization of zinc sulphide as a luminescent material depends, requires optimum non-stoichiometry. It should also be reproducibly. None of the methods hitherto known claim the obtainability of graded non-stoichiometry depending on easily controllable experimental parameters.

In this background the object of this invention is to work out an easy method of obtaining zinc sulphide phosphor avoiding uncertainties factors not easily controlled due to gas (hydrogen sulphide) reaction with the solution phase. Incidentally another aim of the invention is to get such a grade of zinc sulphide phosphor which will be able to work as a good matrix for a phosphor that gives luminescence after doping with the appropriate chemical constituents to obtain the required luminescence.

According to the present invention, there is provided a process for the preparation of phosphor grade zinc sulphide material by reacting an aqueous zinc salt solution with an organic thio compound such as thiourea thioacetamide or the like soluble in water in a pH range of 10-13.

Aqueous solutions of a zinc salt and thiourea in a medium of alkali such that the pH lies between 10 and 13, throw out zinc sulphide precipitate whose yield and non-stoichiometry depend on the pH of the medium yields of zinc sulphide and the degree of non-stoichiometry are fairly reproducible.

The zinc sulphide samples obtained by this new method are not only reproducible in regard to the yield but are also reproducible in regard to their physical properties like non-stoichiometry which is assessed by the magnetic susceptibility values of the precipitated zinc sulphide samples. Secondly, the quality of zinc sulphide obtained is such that even due to non-stoichiometry or due to cold activation which is a process by which the zinc sulphide is suspended in an aqueous solution of a low concentration of the required activating ion, exhibits luminescence. This is not normally so when prepared by other methods, as for example, by the reaction between the aqueous solution of a zinc salt and ammonium sulphide. Preparation of zinc sulphide by this new method having physical properties which are optimum for further sensitization to get luminescent phosphor of zinc sulphide is our new invention in which it is seen to be workable at ordinary temperatures in a single stage and in liquid solutions whose concentrations are all in our control.

The purity of the zinc salt as a starting material is not very critical by this method. In such a case it is possible to get pure zinc sulphide by proper control of experimental conditions.

The present invention provides a process for preparing zinc sulphide directly useful as a luminescent phosphor by a slight subsequent processing. This comprised of a reaction between a zinc salt and an inorganic sulphur compound like sodium sulphide, hydrogen sulphide etc. wherein the H_2S or sodium sulphide is replaced in the present invention by an organic sulphur compound like thiol, thiourea, substituted alkyl thioureas, thioacetamide, or some inorganic thiocompounds like sodium thiosulphate in aqueous solutions at the laboratory temperature and then adjusting the pH to be on the alkaline side around 10-13 in order to get the precipitate of zinc sulphide by the addition of a strong alkali. The precipitation is near completion in about an hour and is hastened considerably to half the time by sufficient stirring. The zinc sulphide thus obtained is of desired properties for use as a starting material for preparing phosphors.

The purity of the zinc salt as a starting material is not very critical by this method. In such a case it is possible to get pure zinc sulphide by proper control of experimental conditions.

EXAMPLE I

The method consists in preparing a 1 M solution of $ZnSO_4 \cdot 7H_2O$, adding an equal volume of 2 M Thiourea solution followed by a strong alkali (about 50% concn.) until the pH of the clear solution so obtained is near about 10.5 at the laboratory temperature. The solution is kept stirred using a magnetic stirrer for about one hour when almost theoretical amount of zinc sulphide is precipitated. Then the contents of the bath are diluted with water, washed by decantation and the precipitate of zinc sulphide is dried at $100^\circ C$ in air oven. The luminescent grade zinc sulphide so obtained is doped with metal ions like Pb^{2+} , Ag^+ etc. by adding the dopant either to the precipitating bath or by the suspension of the zinc sulphide powder in a dilute solution of the dopant for the required period. The doped material so obtained is found to exhibit photoluminescence as reported in literature.

EXAMPLE II

Sufficient quantity of zinc oxide is dissolved in 100 cc of 2.5 to 5 N acetic acid followed by twice the weight of solid thiourea such that the clear solution so obtained must have a pH around 4.5. A strong alkali (30% solution) is added to the above solution until its pH reaches 13 and the solution is kept for 1 hour at room temperature. While zinc sulphide is precipitated which is filtered off after washing several times by decantation until free from alkali. The precipitate is dried at $100^\circ C$ and the zinc sulphide powder so obtained is doped with metal ions like Pb^{2+} , Ag^+ etc. The doped material is found to exhibit the photoluminescence as reported in literature.

EXAMPLE III

A saturated solution of ZnO in strong alkali (approximately 40% concn.) is prepared. Its pH was near about 13. A saturated solution of thiourea, twice that of zincate solution by volume is added and the mixture is kept stirred for one hour using a magnetic stirrer. The precipitate zinc sulphide is filtered off, washed thoroughly with distilled water and dried. The phosphor grade zinc sulphide powder is activated with Pb^{2+} , Ag^+ etc. and the products are found to exhibit photoluminescence as reported in literature.

The main advantages of the invention are :

- (a) The process of precipitating zinc sulphide is done in aqueous solutions using organic thiocompounds in place of inorganic sulphides like sodium sulphide or hydrogen sulphide in hitherto known methods in a range of pH between 10 and 13 and it is possible to control the yield and non-stoichiometry of the precipitated zinc sulphide compounds.
- (b) The zinc sulphides thus obtained can be used straight as the starting material for preparing luminescent phosphors by usual methods of sensitization.

Zinc sulphide used as the starting material for subsequent sensitisation as a luminescent phosphor is known to be prepared hitherto by the reaction of an aqueous zinc salt solution with hydrogen sulphide gas bubbling through the solution. Here the preparation of pure hydrogen sulphide for bubbling through zinc salt solution involves a train of traps, control of rate of bubbling in addition to the criticality involved in choosing the pH of the solution at an optimum.

The present invention uses an organic thiocompound in aqueous solution which simplifies the control of concentration and the concomitant cumbersome procedure involved in conducting the gas-solution reaction. By merely controlling the pH of the bath the yields and the degree of non-stoichiometry could be achieved in the zinc sulphide precipitate. Such precipitated zinc sulphide has been found to be useful without further processing as the starting material for producing luminescent phosphors unlike the case in the conventional method. The reaction is performed at ordinary temperatures.

- (i) The conventional process of reacting an aqueous zinc salt solution with gaseous hydrogen sulphide bubbled through it is modified by substituting hydrogen sulphide with an organic sulphur compound soluble in water.
- (ii) The zinc sulphide samples prepared by this method are controllable in regard to their nonstoichiometry and are useful straight to be the starting material for the preparation of luminescent phosphors.
- (iii) Even if small quantities of unwanted impurities are present in the zinc salt when starting with, it is possible, by a suitable change in experimental conditions to get the same grade of zinc sulphide as obtained when taking analytically pure zinc salt.
- (iv) This invention involves only one step (reaction) to obtain pure zinc sulphide in comparison with a similar method reported in literature by Russian investigators, performed in two stages and involving a higher temperature.
- (v) We claim a process of precipitating zinc sulphide by a new method at the laboratory temperature.

We Claim :

1. A process for the preparation of phosphor grade zinc sulphide material useful for luminescent devices by reacting an aqueous zinc salt solution with an organic sulphur compound such as thiourea, thioacetamide or the like soluble in water.
2. A process as claimed in claim 1 carried out at the laboratory temperature.
3. A process for the preparation of phosphor grade zinc sulphide material useful for luminescent devices substantially as hereinbefore described.
4. Phosphor grade zinc sulphide material which can be used as a starting material for further processing into a luminescent material with desired non-stoichiometry whenever obtained according to a process substantially as hereinbefore described.

(Signed Illegible).

Patents Officer

Council of Scientific and Industrial Research.

Date: this 27th day of January, 1971.