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PREPARATION OF PHOTOCONDUCTIVE MATERIAL

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This invention relates to a photoconductive material and method of preparation thereof, the object being to provide a material which is particularly desirable for use in a radiation amplifier.

Ordinarily, such an amplifier is referred to as a light amplifier, but the more generic expression is used herein, since the material presently involved can be activated not only by visible radiation but by X-rays, beta rays, gamma rays, etc. The term "photoconductive" should be interpreted accordingly.

In practice, photoconductive material is associated with luminescent material and is subjected both to radiation of the character indicated and to an electrical field, whereupon the luminescent material is excited to luminescence according to an electrical pattern established by radiation reaching the photoconductive material, usually through a screen or around an object having portions opaque to the radiation. The result is to multiply the number of electrons emitted by the photoconductive material and reaching the luminescent material, whereby more photons are emitted by the luminescent material than would be emitted if such material were directly irradiated. A shadowgraph pattern of radiation will, therefore, give a much brighter image than would otherwise be possible.

Ordinarily, the photoconductive material and the luminescent material comprise superimposed layers and the pattern of photons emitted as the result of irradiation of selected areas of the photoconductive material may either be viewed directly or used to expose a photographic emulsion.

By reason of the method hereinafter described, the photoconductive material herein disclosed is better adapted for this work than any previously known material, principally because I have discovered how to activate cadmium sulfide with copper in a manner which produces a microcrystalline lattice.

My method as preferably practiced is as follows:

Starting with amorphous cadmium sulfide, desirably having total impurities not more than a few parts per million, a small amount of copper activator is added. The copper activator should desirably be soluble. Copper chloride, copper nitrate, copper acetate or copper sulphate are suitable separately or in mixture. The cadmium and copper salt or salts are thoroughly mixed and desirably comprise small particles. Either dry mixing or mixing in a water slurry will be effective. Desirably (but not necessarily) flux such as potassium or sodium chloride is added and mixed with the other ingredients. Dry mixing may conveniently be done in a ball mill or otherwise. Alternatively, such a mill may be used to reduce the particle sizes of material which has been dried following mixing in a slurry. The sizes or particles of component materials of the final mixture desirably do not exceed about five microns.

The mixture is then heated to a very high temperature in an atmosphere of an inert gas. Provided the particle size of the component materials is small, the extent to which the mixture is heated will control the size of the resulting crystals. The bottom limit for practical purposes is about 800° C. A good quality product is obtained at 1000° to 1150° C. For example, I prefer heating in an inert gas atmosphere for one hour at about 1120° C. There is no top temperature limit except the point where the crystals become too large for practical use.

The copper fuses into the cadmium sulfide lattice (the word "fusing" commonly includes the phenomenon of migration) at the temperatures indicated and upon cooling is tightly bound in the cadmium sulfide crystalline lattice. After being cooled, the mixture is crushed, as in a ball mill or with mortar and pestle, to reduce the materials to a fine powder without destroying the microcrystalline structure. Grinding should be kept to a minimum. The resulting particles are washed free of such activating copper salts and flux as are not bound in the lattice. This may be accomplished with water alone although a dilute solution of potassium or sodium cyanide aids in the removal of the excess copper.

After the fired material has been washed and dried, it is very slightly oxidized. This may be accomplished successfully by dusting very thin layers of the powder onto glass sheets and heating in oxygen or air. Neither the temperature nor duration of the heating is particularly critical, but best results have been observed within the range of 400° to 600° C. The resulting powder is highly photoconductive and particularly suitable for use in radiation amplifiers. Samples have been prepared which have a light-to-dark photocurrent ratio greater than 10^7 at 2 foot candles. Apparently each particle of the powder comprises a lattice of the cadmium and copper salts upon which cadmium oxide is coated.

A specific example of preparation is at follows: 30 cc. of a solution containing 0.001 gram $Cu^{++}/cc.$ as $CuCl_2$ and 20 cc. of a solution containing 0.1 gram NaCl/cc. are added to 100 grams of cadmium sulfide. This is uniformly mixed and then dried. After drying, the CdS with $CuCl_2$ and NaCl is further mixed and reduced to small particle size. After thorough mixing, the powdered mixture is heated to 1120° C. for one hour in an atmosphere of nitrogen. After cooling it is crushed to a fine powder and washed with 2% KCN and hot water, and dried. The dry washed powder is dusted onto glass sheets in thin layers and heated in air for fifteen minutes at 500° C. The resulting powder is highly photoconductive.

The highest photoconductivity of the powder prepared as above appears to be in the range of orange light of about 6000 Angstroms. However, many other combinations of activator concentration, firing temperature and firing time may be used and the resistance of the powder may be varied to suit particular applications by varying the copper concentration, the firing temperature and the firing time.

The table below shows characteristics of typical samples of photoconductive cadmium sulfide composition prepared in accordance with the method above disclosed. The table also indicates ranges which have been found most desirable in the compositions used and the firing temperatures employed and the voltages applied.

Sample Composition	Firing Temp., ° C.	Applied Voltage, v.	Current at 2 ft. c., Tungsten 10 sec. after irradiation, μa.	Current in dark, 10 sec. after irradiation, μa.
100 CdS:.03 Cu:2 NaCl	1,060	300	2,000	.02
100 CdS:.03 Cu:2 NaCl	1,120	150	2,000	.02
100 CdS:.01 Cu:2 NaCl	1,120	100	2,000	1
100 CdS:.005 Cu:2 NaCl	1,120	100	2,000	50

For the purpose of the tests reported in the foregoing table, the samples tested were made by suspending cadmium sulfide powder in a dielectric and placing it between two electrodes 5 mils apart and covering a small area in the order of 0.4 square inch.

Work with cadmium sulfide crystals of large sizes has been done in this field, but the present procedure results in the formation of a microcrystalline structure having great advantages. The formation of the microcrystalline structure is believed to be attributable to the firing of small size particles of the starting material within the specified range of temperature. The copper causes the photo-sensitivity and the presence of the chloride helps to incorporate the copper in the lattice.

Photoconductive layers of this powder may be made in any desired size or shape by ordinary techniques of spraying, settling or silk-screening. The small size of the crystals and the small crystal aggregates of the resulting powder are very advantageous in this regard. The technique of preparation is much simpler than that required in the preparation of photoconductive large single crystals or vapor-deposited layers. The results are much more readily reproducible with accuracy than by any previously known method. Moreover, it is advantageous to be able to vary electrical resistance to suit different applications.

This powder has made it possible to construct a solid state image amplifier which, without it, was proving difficult of development.

I claim:

1. The method of preparing a photoconductive material which comprises mixing 100 gms. of cadmium sulfide with a solution of .001–.03 gm. of a copper salt and .1–.2 gm. of an alkali chloride flux, heating the mixture to a temperature of 800–1150° C. and in an inert atmosphere to crystallize the cadmium sulfide and bind copper into the crystal lattices, crushing the material without destroying the cadmium sulfide crystal structure, washing the unbound copper and its salt and the flux from the material, and heating the crystals at 400–600° C. in an oxidizing atmosphere up to 15 minutes for oxidizing the crystal surfaces to a very slight degree.

2. The method of preparing a photoconductive material which comprises mixing in the proportion of 100 gms. of cadmium sulfide with a solution of .001–.03 gm. of a copper salt and .1–.2 gm. of an alkali chloride flux, heating the mixture to a temperature of 800–1150° C. for up to one hour in an inert atmosphere to crystallize the cadmium sulfide and bind copper into the crystal lattices, crushing the material without destroying the cadmium sulfide crystal structure, washing the unbound copper salt and the flux from the material, and heating the crystalline material in an oxidizing atmosphere at 400–600° C. up to 15 minutes for oxidizing the crystal surfaces.

3. The method of claim 2 in which the first heating step is at approximately 1120° C. for about one hour and the second heating step is at approximately 500° C. for about 15 minutes.

4. The method of preparing a photoconductive material which comprises mixing cadmium sulfide with a copper salt and an alkali chloride flux in the approximate proportions of 100 parts to .001–.03 part and .1 part respectively, reducing the mixture to small particle size, heating the mixture to a temperature in the range of 800–1150° C. in an inert atmosphere to crystallize the cadmium sulfide and bind copper into the crystal lattices, crushing the material without destroying the cadmium sulfide crystal structure, removing the unbound copper salt and the flux from the material, and heating the crystalline material in an oxidizing atmosphere at a temperature in the range of 400–600° C. for about 15 minutes for oxidizing the crystal surfaces.

5. The method of claim 4 in which the mixture is reduced to no more than 5 microns particle size.

6. The method of claim 4 in which the final particle size is reduced to less than 5 microns.

7. The method of preparing a photoconductive material which comprises mixing 100 gms. of cadmium sulfide with a solution of .001–.03 gm. of a copper salt and .1–.2 gm. of an alkali chloride flux, drying the mixture, reducing the mixture to a particle size of no more than 5 microns, heating the mixture to a temperature in the range of 800–1150° C. up to an hour in an inert atmosphere to crystallize the cadmium sulfide and bind copper into the crystal lattices, cooling the material, crushing the material without destroying the cadmium sulfide crystal structure, washing the material with a solution of an alkali cyanide to remove the unbound copper salt and the flux, and heating the material in air at a temperature in the range of 400–600° C. for about 15 minutes for oxidizing the cadmium sulfide crystal surfaces.

8. The method of preparing a photoconductive material which comprises mixing cadmium sulfide with a solution of a copper salt in the approximate proportions of 100 gms. to .001–.03 gm. and with about .1 gm. of an alkali chloride flux in solution, reducing the mixture to particle size of no more than 5 microns, heating the mixture in an inert atmosphere at a temperature of approximately 1120° C. for about 1 hour to crystallize the cadmium sulfide and bind metallic copper into the crystal lattices, crushing the material without destroying the cadmium sulfide crystal structure, washing the material with a dilute alkali cyanide solution to remove the unbound copper and its salt and the flux and heating the material in thin layers in air for about 15 minutes at a temperature of approximately 500° C. for oxidizing the cadmium sulfide crystal surfaces.

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