JOURNAL OF MATERIALS SCIENCE **33** (1998) 471–476

ZnS precipitation: morphology control

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ZnS is the most important base material for cathode-ray tube luminescent materials. In order to meet the requirements of various types of luminescent screen, routes to ZnS powder with adjustable particle morphology were investigated. The most important morphological parameters of ZnS phosphors are the particle size and the particle size distribution. Industrially, ZnS synthesis is performed by precipitation in an aqueous medium. Precipitation methods included in this study are homogeneous precipitation, precipitation in liquid crystal phase and the introduction of seeds. The powders received were processed to luminescent materials in a standard manner. The results are discussed in relation to raw ZnS powder properties as well as to the morphology and performance of the resulting annealed phosphor powders. From the methods investigated, the use of seed sols based on nanosized CuS, ZnS and S particles yielded the best results, namely, well-defined phosphor particles of micron-scale diameter.

1. Introduction

ZnS-based luminescent materials (phosphors) are the most important for cathode-ray tubes (CRTs). In consumer sets as well as in computer monitors, the blue and green primary colours are generated by ZnS phosphors. These phosphors are applied in the form of powders. They are industrially synthesized in a three-step process: after precipitation of raw ZnS in aqueous solution, this starting material is mixed with precursors of the (activator and coactivator) dopants and then fired to the final (now luminescing) phosphor powder. Depending on the application, some modification of the grain surface may follow (in order to comply with the technology used for the screen-manufacturing process).

The quality of the final screen in terms of homogeneity and resolution is determined to a large extent by the powder morphology. In general, particles with a mean diameter between 1 and 10 μm (depending on the screen type) and a narrow particle size distribution are required. The particle shape should be spherical in order to prevent texture effects on the screen. The final size of the particles is generally tuned during the high-temperature step with the aid of fluxing agents. The minimum size and the resulting particle shape on the other hand are pre-set by the starting material for the firing step (namely, precipitated ZnS). Since fluxing serves only to grow the pre-set ensemble of raw material particles, a very-well-defined starting material is required. This means a controlled particle shape as well as the exclusion of unwanted particle agglomeration. Because of a general tendency towards the use of smaller phosphor particles and improved screen packing, efforts to prepare dedicated raw material have been stimulated.

Since, at particle diameters below 1 μm, phosphors drastically lose their luminous efficiency, this size is the practical lower bound. The final goal is therefore the precipitation of small, compact, spherical and well-separated particles with low sintering activity, yielding phosphors with a mean particle size of around 1 μm. Larger types of phosphor could then be prepared from such materials by the use of fluxes promoting particle growth.

Prototype techniques used for this purpose studied in this work are the well-known homogeneous precipitation techniques (thioacetamide as sulphide source), precipitation in liquid crystal phase and the use of sulphide and sulphur nanoparticles as seeds.

Application of precipitated ZnS as a phosphor raw material requires conservation of shape during the heat treatment necessary (typically 900–1000 °C). Upon firing at this temperature, the grain is densified first and loses its internal structure. This coalescence phase takes some 5–10 min [1]. Thereafter particle growth via sintering, vapour transport or fluxing takes place [2]. Test firing for shape conservation therefore was (without any fluxes or additives, but under coal powder to exclude oxygen) for 15 min at 950 °C. Efficient ZnS phosphors are preferably of sphalerite structure. Therefore firing temperatures must be below 1000 °C and the raw material must not have any tendency to exhibit the (under these conditions metastable) wurtzite structure.

The use of thioacetamide as sulphide precursor has extensively been exploited for the preparation of monosized ZnS particles [3]. The decomposition kinetics of thioacetamide to H_2S can be controlled by the pH and the temperature (a low pH and a high temperature promote H_2S formation). Although the

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particles prepared this way can be almost perfectly spherical, they show an internal structure (indicating participation of agglomeration steps or continuous homogeneous precipitation); thus the detailed mechanism is still under debate [4–8]. In this work, the method has been extended to coprecipitation of CuS together with ZnS. Because of the lower solubility of CuS, CuS is expected to precipitate first and to form nucleation seeds for subsequent ZnS precipitation. The amount of Cu coprecipitated is the same as required for activation of ZnS to a luminescent material mole fraction of Cu typically 10^{-4}–5×10^{-4} (100–500 molppm)].

Reverse micelles have been shown to be a very effective medium for the controlled precipitation of nanosized even-structured semiconductor particles [9]. This concept of arrested precipitation can be extended to liquid crystal phases. Precipitation can then occur inside the channel or void system of the liquid crystal. The restricted geometry serves as a medium for arrested precipitation and may yield very uniform particles, sometimes in modifications not accessible in a purely aqueous medium [10].

This study will present results from work with sodium dodecyl sulphate (SDS) and Tween® 80 (polyoxyethylene(20)-sorbitane monooleate) as prototypes. Excluding the influence of the electrolytes dissolved, the phase diagrams for the mixtures of these surfactants with water were taken from [11] and [10], respectively.

The role of the seeding stage to control ZnS precipitation has been discussed in the literature concerned with homogeneous precipitation [4, 7, 8, 12]. In this work, seeds were prepared separately in an organic medium and then transferred into the precipitation solution. Seed sol preparation followed a procedure described in the literature [13]. ZnS or CuS particles with diameters between 10 and 20 nm can be prepared as a fairly stable colloid suspension in dimethyl formamide (DMF). This seed suspension is then transferred into aqueous medium. Alternatively, sulphur sols were prepared by mixing a saturated solution of sulphur in acetone with the precipitation solution.

2. Experimental procedure

2.1. Homogeneous precipitation

Experiments with thioacetamide (TAA) were performed with aqueous, membrane (200 nm)-filtered $Cu(NO_3)_2$–$Zn(NO_3)_2$–thioacetamide solution by heating to 80 °C for approximately 4 h under stirring (Zn, 27.4 mmol l^{-1}; Cu, 5.26 µmol l^{-1}; TAA, 103 mmol l^{-1}). The pH was set to 3.5 by the addition of nitric acid. The product was isolated by filtration, washed with water and alcohol and dried for several hours at 100 °C.

2.2. Precipitation in liquid crystal phase

$ZnSO_4$ stock solution (0.6 mol l^{-1}) was filtered through 200 nm membrane filters. The highly viscous starting "solution" was prepared by mixing at elevated temperatures (45 wt% in case of SDS, and 50 wt% with Tween® 80) and subsequent cooling to room temperature in the reaction vessel (gas-tight flask). The precipitation was performed by passing gaseous H_2S (flow rate about 60 sccm) over the solid mass at room temperature. After purging from the H_2S gas, the product was isolated by melting of the liquid crystal mass and dilution with water. A typical reaction time was 6 h for 0.15 mol of $ZnSO_4$ reacted. The material was isolated by filtration, washed with water and alcohol and subsequently dried for 24 h at 100 °C.

2.3. Precipitation on CuS seeds

Seeds of CuS were prepared from solutions of anhydrous Cu(II) acetate (2 g) in dry DMF (150 ml) (73 mmol l^{-1}). H_2S (750 ml at ambient pressure, diluted with Ar(1: 1)) was passed through this solution in 90 min. The product was filtered through a 200 nm membrane. The clear green–black colloidal solution formed this way was stored at -20 °C. The sol concentration was determined by evaporation and weighing. Aliquots of the sol were transferred under vigorous stirring to a $ZnSO_4$ (0.6 mol l^{-1}) stock solution in a gas-tight flask. Precipitation was immediately started by passing H_2S gas over the continuously stirred solution (about 60 sccm). H_2S was used in 1.5-fold stoichiometric surplus. The precipitated material was isolated by filtration, washed with water and alcohol and subsequently dried for 24 h at 100 °C.

2.4. Precipitation on ZnS seeds

ZnS seeds were prepared in the same way as CuS seeds, using dry Zn acetylacetonate (85 mmol l^{-1}) dissolved in dry DMF. To speed up dissolution, warm DMF (70 °C) was used. Depending on the water content of the DMF used, the clear yellow colloidal ZnS solution formed this way after membrane filtration contained typically ZnS at 60 mmol l^{-1} (about 70% yield). The sol could be stored at -20 °C for 24 h without visible flocculation. Precipitation of ZnS on ZnS seeds proceeded as described for CuS seeds. Because of the lower stability of the ZnS sol, however, only freshly prepared seed sols were used.

2.5. Precipitation on S seeds

A saturated S solution in acetone was prepared by boiling acetone over solid sulphur under reflux and storing it at room temperature over solid sulphur. The S concentration at room temperature was then determined by evaporation and weighing. Depending on the water concentration in the acteone used, a typical concentration was 2.5 mmol l^{-1}. From this solution, the required amount was transferred to the precipitation solution under vigorous stirring, immediately followed by the start of the precipitation run (under conditions as described for precipitation on CuS seeds).

2.6. Processing the precipitate to luminescent powder

If necessary, dopants (Al and Cu) were added to the precipitate by adding them as nitrates to a slurry of the precipitate in water, followed by solvent evaporation and drying at 100 °C. The nominal concentration of Al was 500 molppm, and of Cu 150 molppm. Fluxes (if present) were introduced at this mixing step as well. Processing of the powders prepared took place in quartz tubes, closed on one side. The powder was covered with powdered charcoal in order to exclude oxygen during firing. Test firing was for 15 min at 900 °C; standard firing to phosphor powders was for 90 min at 980 °C. After firing, the phosphors were quenched by dipping the quartz tubes into water.

2.7. Characterization

Particle sizes were determined by scanning electron microscopy (SEM) inspection, by Coulter counter measurement or in a CIS-GALAI laser inspection system. Transmission electron microscopy (TEM) pictures of the sol particles were taken by collecting particles from the undiluted sol on a mesh. Scanning electron micrographs were taken by standard techniques (sputtering with Au). The Brunauer–Emmett–Teller (BET) surface was determined by the standard technique, using N_2. The crystal structure was determined from the powder diffraction patterns. The luminous efficiency was determined under electron beam excitation with a calibrated photometer. Emission spectra were recorded with an optical multichannel analyser system under electron beam excitation.

3. Results and discussion

3.1. Homogeneous precipitation

In accordance with the literature, monosized spherical submicron ZnS particles could be prepared, both with Cu coprecipitation and without. Fig. 1a and b shows scanning electron micrographs of the material as precipitated and after test firing (15 min at 900 °C), respectively. Obviously the shape as determined by the precipitation procedure can be retained during firing. This indicates that the concept of shaping the raw material to get a perfect phosphor powder holds, since well-separated precipitated particles show a sufficiently small sintering activity. However, comparison of material precipitated without Cu addition and with Cu coprecipitated revealed that without Cu coprecipitation it is very difficult to receive pure sphalerite material after annealing. Only with Cu present is sphalerite formed readily. It remains unclear whether this behaviour is an effect of Cu seeds precipitated first in the course of the reaction or whether it is simply an effect of Cu being incorporated continuously.

However, attempts to scale up the process in a sensible way showed that perfect particles are formed in dilute solution only. A more concentrated starting solution could not be controlled in an easy way. Moreover, the precipitated material contains large amounts of organic residue, which is hardly removeable.

The fired powder therefore is greyish (caused probably by carbon inclusion) and thus has a decreased luminous efficiency. Moreover, since only with Cu coprecipitated the desired phase purity could be achieved, the material could of course only be used for Cu-activated ZnS luminescent material. For these reasons (although the particles prepared are on the desired geometrical scale), use of this variant of homogeneous precipitation for industrial production of ZnS does not seem to be feasible.

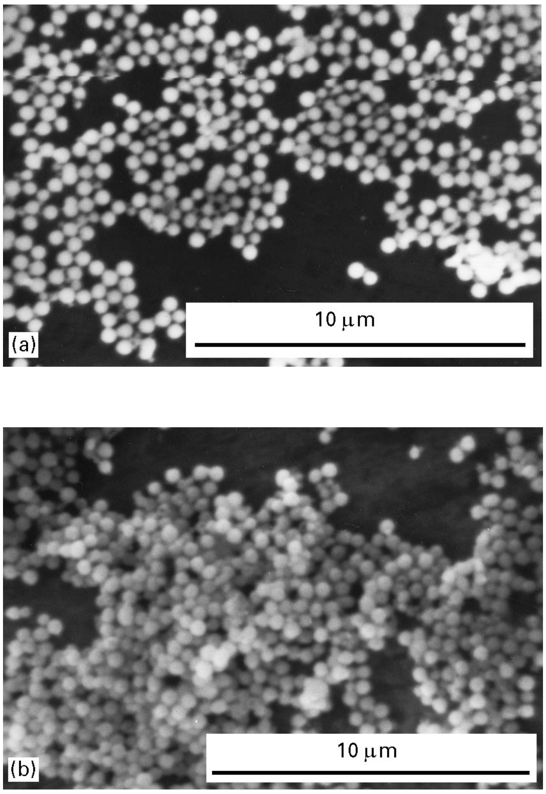


Figure 1 Scanning electron micrographs of ZnS particles precipitated homogeneously with thioacetamide as the sulphide source: (a) as precipitated; (b) after test firing at 900 °C for 15 min.

3.2. Precipitation in liquid crystal phase

Fig. 2 shows ZnS powder precipitated in the hexagonal liquid crystal phase of the SDS–H_2O system (at 45 wt% SDS). The particles are very well separated and spherical and cover a size range from 0.2 to 1 μm. Obviously, precipitation inside the aqueous channel system of the liquid crystal (restricted geometry) is well suited to the preparation of small well-defined spherical particles. Attempts to employ the lamellar liquid crystal in the SDS–H_2O–$C_5H_{11}OH$ system did not yield the desired spherical particles, but rather a dense agglomerate.

Tween® 80 also exhibits a liquid crystalline phase in the system with water (at 50–60 wt%). Precipitation from the liquid crystal phase (Fig. 3) yields loosely agglomerated particles of diameter around 0.7 μm. Although the size distribution is quite narrow, no such well-separated particles as with the hexagonal SDS liquid crystal were formed.

When it came to processing of the material precipitated in the presence of surfactants to luminescent powder, the samples showed considerable problems with organic residue. Owing to the strong adsorption of the surfactant to the powder particles, it is not possible to get rid of them by simple washing. Oxidative destruction on the other hand is not

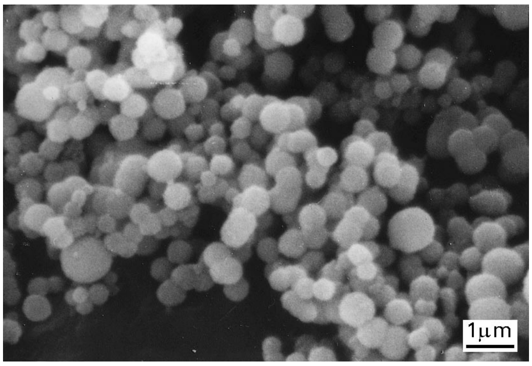


Figure 2 Precipitate from hexagonal SDS–H_2O liquid crystal (45 wt% SDS).

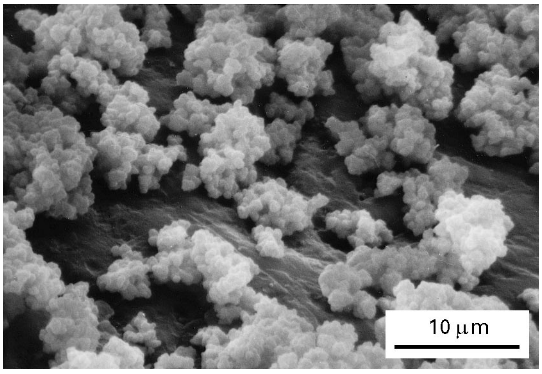


Figure 3 Precipitate from the (hexagonal) liquid crystal phase in the Tween® 80–water system.

recommended because of the danger of damage to the ZnS itself. Processing ZnS to a phosphor takes place basically in a sulphidic atmosphere; under these conditions the organic material is not burnt away quantitatively, but it can rather give rise to partial reduction of the ZnS and incorporation of carbon. Both effects yield (greyish) material not suitable for preparation of high-quality luminescent materials.

3.3. Seeds

Seed sources for this work were ZnS and CuS sols (prepared in DMF) and aqueous S sols. The CuS sol is the most stable in this series. Fig. 4a and b gives an example of H_2S-precipitated ZnS using CuS seeds in an amount necessary for phosphor doping (150 mol ppm) and of the fired material (980 °C; 90 min; no fluxes), respectively. On mixing the CuS seed sol with the $ZnSO_4$ solution, a clear greenish liquid is obtained. Immediately after exposing it to H_2S gas, ZnS precipitation starts (the liquid gradually becomes turbid). No induction period is observed. The resulting powder has a high BET surface (about 50 $m^2 g^{-1}$, at typical agglomerate diameters of 500 nm), demonstrating the internal structure of the particles. After addition of Al and firing, the powder exhibits a pure sphalerite structure and intense green luminescence.

Although the material has the desired particle size after firing and a narrow particle size distribution, the correlation with the special morphology of the freshly precipitated ZnS is not clear. From inspection of the scanning electron microscopy (SEM) picture (Fig. 4) and from BET measurement, the precipitate obviously consists of smaller subunits. The agglomerates seen on the other hand have a quite specific size but are considerably smaller than the final particles after firing. A simple "one-seed–one-particle" mechanism cannot account for these phenomena. Most probably, a combination of seed growth and (hetero) coagulation is encountered, which in a comparable form has also been proposed for the formation of monospheres in the homogeneous precipitation route [8]. The agglomerates formed on the other hand are quite dense already, such that the sintering activity between particles is low. Therefore, particles with a relative narrow size distribution are formed during the heating step. Since the size distribution is narrow also for the precipitated agglomerates, no growth of larger particles occurs; only the very small particles are consumed.

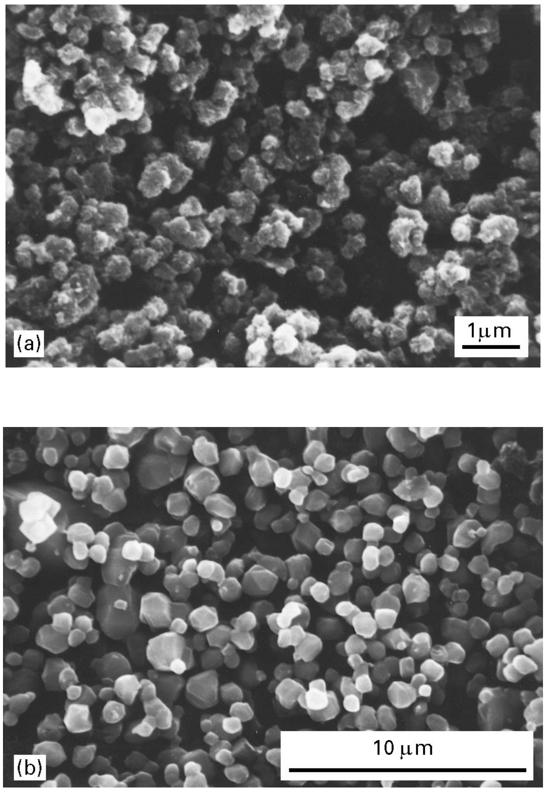


Figure 4 Precipitated ZnS on CuS seeds: (a) as prepared (b) after firing to phosphor powder.

Comparable results have been achieved by using ZnS seed sols. Additionally, the particle size of the seeds has been checked in this case by TEM measurement to be of the order of 10–20 nm which is of the same order of magnitude as reported for CuS [13]. As with CuS seeds, firing yields pure sphalerite phase material.

The necessary amount of ZnS to be introduced for seeding is on the same scale as in the case of CuS (expressed in millimoles of seed per litre of reaction solution). In either case only a few millilitres of DMF are introduced per litre of reacting $ZnSO_4$ solution; they appear to be washed away or burnt off completely, yielding luminescent materials with luminous efficiency and luminescence colour close to or equal to

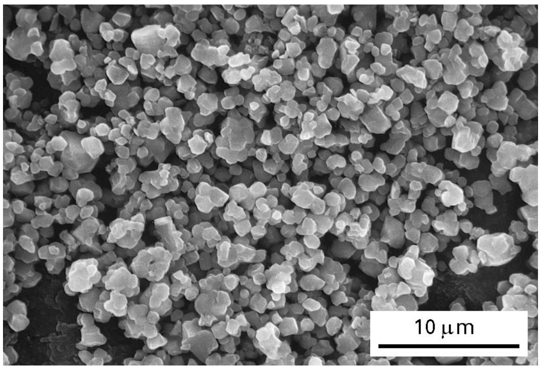


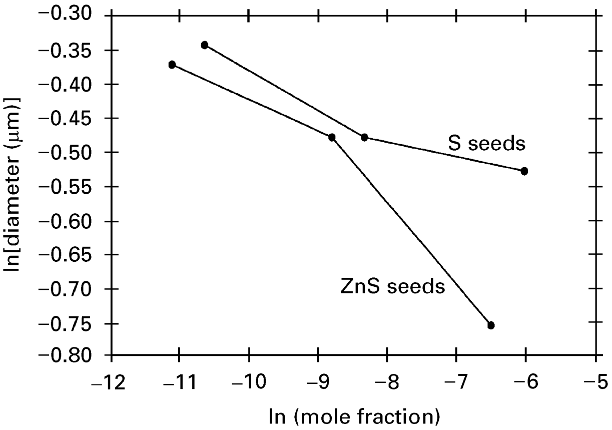
Figure 5 SEM picture of precipitated ZnS on S seeds after firing to phosphor powder.

standard materials (grown with fluxes to larger grain size). However, when using excessive amounts of DMF (in other words, very dilute seed sols), a tendency of the ZnS powders to acquire a greyish body colour has been observed.

S colloids for seeding are extremely simple in their preparation (basically pouring saturated S solution in acetone under vigorous stirring into the reaction solution) but badly defined, since their colloidal state is not stable; the size and size distribution of the colloid are therefore dependent on the details of the preparation. Since the particle size of the colloids was expected to be on the same size scale as the sulphides made in DMF (10–20 nm), the molar concentration of S introduced as seed was in the same range (50–200 mol ppm). Despite the rather poor control over colloid formation, the results, as far as particle morphology is concerned, are satisfying. Fig. 5 shows the scanning electron micrograph of a luminescent powder prepared this way. The material is of a pure sphalerite phase. The route over S colloids needs comparatively large amounts of acetone; this solvent, however, is easily removable.

As already remarked above, no simple "one-seed–one-grain" mechanism for particle growth during precipitation can be expected. This is demonstrated in an attempt to vary the primary particle size by varying the amount of seeds. In an idealized picture, the precipitate particle diameter would be proportional to the inverse of the third root of the seed concentration. Fig. 6 shows the relation as measured with ZnS and S seeds from a concentration series in a double-logarithmic plot (diameters estimated from SEM pictures). A linear fit to this plot yields a slope of – 0.04 for the S seeds and of – 0.08 for the ZnS seeds, both values being far away from the theoretical value of – 1/3. Obviously, coagulation phenomena besides simple growth are present.

The materials prepared via the seed sol routes described above yield powder particle diameters of 1–2 μm when fired to a luminescent material. This size can be increased by the addition of suitable fluxes (halogenides of alkali metals, earth alkali metals or zinc). Fig. 7 shows particle size distributions of powders received by firing with and without fluxing with iodides, using raw material precipitated on CuS seeds. Firing with fluxes in general not only increases the particle sizes but also improves the crystal quality and/or phase purity of the particles. For phosphors, this means an increase in luminous efficiency, because some of the non-radiative de-excitation channels vanish by this treatment. The powders prepared from ZnS precipitated on seeds then exhibit luminous efficiency and colour equal to standard materials.



Seed type	Mole fraction (seeds)	Diameter (μm)
S	2.4×10^{-5}	0.71
S	2.4×10^{-4}	0.62
S	2.4×10^{-3}	0.59
ZnS	1.5×10^{-5}	0.69
ZnS	1.5×10^{-4}	0.62
ZnS	1.5×10^{-3}	0.47

Figure 6 Dependence of precipitate agglomerate size (diameter) on seed concentration.

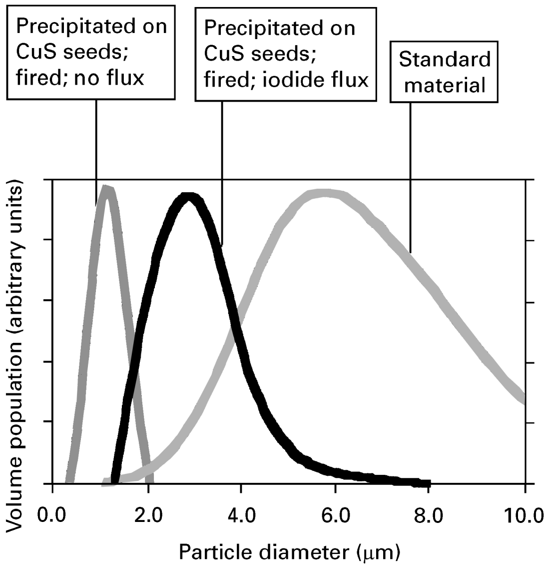


Figure 7 Particle size distributions of ZnS received by precipitation on CuS seeds after firing with and without fluxing agents, compared with standard material (volume statistics).

Summarizing, model reactions aiming at the size and shape control of ZnS phosphor powder have been performed. Monosized ZnS particles have been prepared by homogeneous precipitation. The shape as induced in the raw material during precipitation was retained in the subsequent high-temperature processing. Organic residue and the need for high dilution make homogeneous precipitation with TAA unfeasible for industrial purposes. Precipitation in the hexagonal liquid crystal channel system of the SDS–water system yielded well-defined particles, but purging them from surfactants proved to be difficult. Direct introduction of seeds (CuS, ZnS and S) of nanosize dimension proved to be a promising way for the size control of the ZnS precipitate. Luminescent powders on the micron scale and above could be prepared with a high luminous efficiency and standard colour. The detailed mechanism behind the action of the seeds remains unclear so far.

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Received 7 May 1996
and accepted 29 July 1997