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A Novel Method for the Preparation of Inorganic Sulfides and Selenides

I. Binary Materials and Group II-VI Phosphors

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A novel method for the synthesis of a wide range of metal sulfides and selenides is described. Polysulfide solutions formed by the dissolution of sulfur in hydrazine monohydrate have been shown to contain the hexasulfide and tetrasulfide anions. The action of these solutions, or their selenium analogues, with a range of transition and main group metal salt solutions yields a precipitate, which after firing at an elevated temperature, forms a crystalline metal sulfide or selenide. This method of preparing metal chalcogenides has been extended to some group II-VI phosphors with promising luminescent properties.

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Metal sulfides and selenides are currently used, or have potential use, for a wide range of technological products in the modern world. Examples include phosphors (in televisions, display devices, and scintillation counters),[1,2] semiconductors,[3a] ceramics,[3b] pigments,[3c,d] IR transmitting windows,[3e] lubrication,[3f] hydrogenation catalysis,[3g] sulfite process wood pulp bleaching,[3h] photochemical solar energy conversion,[3i] photodetection,[3j] high temperature batteries,[3k] photovoltaic cells,[3l] and nonlinear optics.[3m]

Such metal sulfides and selenides are presently prepared by a range of methods including the interaction of sulfur or selenium with metals,[4a] the action of a sulfurizing atmosphere at elevated temperature on a metal salt,[5] and wet chemical methods. Examples of the latter are precipitation with carbon disulfide or ammonium sulfide,[1] reduction of metal sulfates/selenates,[6] decomposition of organosulfur compounds such as selenourea,[7] or thioacetamide,[3c] or by sol-gel methods utilizing organic thiols rather than alcohols.[8]

However it has always been very difficult to precipitate pure and stoichiometric metal sulfides, due to anionic impurities particularly hydroxides (which form oxides at high temperatures).[1] For some uses, such as phosphors, contaminants, either anionic or cationic, can drastically alter the performance and possibly the color of the emission, therefore the preparation of highly pure materials from readily available reagents is particularly important in this field.[1] In addition, the current ecological demands necessitate that future preparation of metal sulfides should not produce high volumes of waste or side products, such as sulfur/selenium containing gases,[9] unlike many of the methods mentioned above, particularly those utilizing a sulfurizing atmosphere (such as H_2S or CS_2 to convert a precursor to a sulfide at elevated temperatures).

Inorganic powder phosphors are highly pure crystalline materials which have been purposely doped with small quantities of other ions (0.01 mol % silver in cathode ray tube (CRT) ZnS:Ag),[1] the precise concentration of the dopant affects the luminescent properties and thus the applications the material is suited for.[2] The presence of other ions, additional to the desired activator, can affect both the color and efficiency of the phosphor produced.[1,2] Examples of these effects are (*i*) the addition of 0.015 mol % aluminum to ZnS:Ag results in a shorter wavelength blue light being emitted (which is desirable), but there is a concomitant decrease in the efficiency of the phosphor[10] (which is not), and (*ii*) the presence of low quantities of iron in ZnS:Ag results in a quenching of the visible luminescence which becomes more dramatic as the iron concentration increases.[2c]

Zinc sulfide activated with silver (ZnS:Ag) has a blue luminescence and is one of the most efficient cathodoluminescent phosphors known.[1,2c] Changing the activator to copper (ZnS:Cu) and other codopants gives a green luminescence.[2c] ZnS phosphors are very widely used. Applications include: CRTs,[2c] electroluminescence,[2d] X-ray fluorescent screens,[2e] scintillation,[2f] vacuum fluorescent displays,[2g] field emission devices (FEDs),[2h] radioluminescent paints,[2i] and phosphorescent pigments.[2i] Activated cadmium sulfide and zinc and cadmium selenide (and mixtures thereof) have also been used commonly as phosphors,[1,2c] though their continued application is now limited by the toxicities of cadmium and selenium, they are still used in radar displays and high resolution storage tubes.[2c]

In a preliminary study it was shown that the action of sulfur dissolved in hydrazine monohydrate on a zinc salt solution could be used to prepare ZnS:Ag phosphors which luminesced at slightly longer wavelengths than commercial materials and had higher efficiencies.[11]

Here we present more detailed and wider ranging results which demonstrate that the reaction of a solution of sulfur or selenium dissolved in hydrazine monohydrate with metal salt solutions provides a versatile and simple method for the preparation of a range of p-block and transition metal sulfides and selenides.

To investigate the nature of the reactive species present in sulfur solutions of hydrazine monohydrate electronic absorption spectroscopic investigations were undertaken, and are discussed with respect to previously reported investigations of electrochemically reduced sulfur in dimethylformamide. The dominant anionic sulfur species in the solutions in hydrazine monohydrate has been identified and the implications of the nature of this species to the synthesis of metal sulfides are discussed.

We have further investigated the use of this method for the preparation of ZnS:Ag and improved on our previous results. In addition we have extended the method to the preparation of other II-VI phosphor materials including ZnS:Cu, zinc sulfoselenide activated with copper ($Zn\{S,Se\}_1$:Cu), and zinc cadmium sulfide activated with copper ($\{Zn,Cd\}_1S$:Cu).

A major advantage of this method is that it limits the quantities of sulfur-containing gaseous by-products evolved during firing, and it is therefore more environmentally friendly than current industrial methods. The method is also quick to use, and (with suitable safety precautions) can be scaled up easily.

Experimental

Reagents were used as purchased, for the preparation of luminescent materials all reagents were of at least AnalaR grade, dopants used were usually of 99.99% purity or higher. 99.999% sulfur (Aldrich) and/or 99.5% selenium (Aldrich) were used. Scanning electron microscopy (SEM) images were recorded using Cambridge Instruments Stereoscan 90, Coulter Counter particle size measurements were recorded using a Coulter Multisizer II attached to a PC, X-ray powder diffraction (XRD) patterns were recorded using a Philips PW1710 diffractometer. A Perkin Elmer $\lambda 3$ spectrometer was used to record the electronic absorption spectra. Cathodoluminescent excitation was achieved under vacuum at around 10^{-6} Torr and a Kimball Physics, Inc. (Walton, NH) model EGPS-7 electron gun. The E-beam used was 1.4 mm in diam and the current 8.5 μA.

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Photoluminescent and cathodoluminescent emission spectra were measured using a Bentham Tel301D detector, DMC3B programmable monochromator control, M300 monochromator, and a 228A programmable current amplifier linked to a PC. Photoluminescent excitation was achieved using a 366 nm wavelength light. Cathodoluminescent emission intensity was measured using a Photo Research Pritchard PR880 photometer.

Stubs coated in the samples for luminescence measurements were prepared by electrophoretic coating. The phosphor (≈0.5 g) was suspended in 5×10^{-4} M $Mg(NO_3)_2$ in IPA (50 mL) and dispersed in an ultrasonic bath. The voltages used to coat the stubs ranged from 2 to 300 V; times used varied to allow coats of similar mass to be deposited for each sample.

Synthetic methods.—The precipitation of metal sulfides and selenides was carried out by an extension of our previously detailed method.[11] Solutions of metal salts were used in concentrations of 0.25 mol dm^{-3} or less. It must be noted that nitrates, perchlorates, carbonates, and other oxidizing anions are incompatible with the strongly reducing hydrazine hydrate, therefore acetates and chlorides were used. Sulfur and/or selenium solutions were prepared by the slow addition of the chalcogenide to cooled (≈0°C) hydrazine monohydrate in air (sealed systems under N_2 atmosphere were avoided to prevent the danger in containment of a rapid gas evolution). In the case of a metal sulfide preparation an excess of the sulfur solution (calculated on sulfur concentration) was then filtered under gravity into the metal salt solution (again open to the air). The resulting precipitate was filtered off, washed with water, then isopropyl alcohol (IPA), and dried. The dry precipitate was then fired under an inert atmosphere in a tube furnace. Table I shows the metal salts used, the firing temperatures, and the phase composition of the fired material.

Luminescent materials were prepared by a similar method, with the addition of known quantities of dopants to the zinc and/or cadmium solutions. The precipitate was intimately mixed with a known quantity of flux, such as NaCl (typically 2 wt %), and sulfur (typically 5 wt %). The mixture was then firmly packed into a silica crucible which was placed inside a larger crucible filled with sacrificial ZnS; the latter ZnS used must be of reasonable purity as metal ions can migrate from this to the inner crucible. The crucibles were heated in a furnace at 900°C for 1 h and then allowed to cool. When cool the material was washed first with 1:1 glacial acetic acid, then water followed by IPA before being dried overnight at 80°C.

Preparation of solutions for electronic absorption spectroscopy.—Solutions were prepared using dry spectroscopic grade dimethylformamide. The dimethylformamide was degassed under vacuum while being agitated by an ultrasonic bath and then flushed with and stored under dry nitrogen before use. All solutions were prepared and manipulated in darkness to avoid photochemical decomposition.[12,13] Solutions containing known quantities of sulfur or hydrazine monohydrate in dimethylformamide were prepared, and these were mixed and diluted with known quantities of dimethylformamide, to the required concentrations, under dry nitrogen. The diluted solutions were allowed to stand for 1 min while color developed prior to being examined by electronic absorption spectroscopy.

Results and Discussion

Synthesis of metal sulfides and selenides.—Table I summarizes the range of main group and transition metal compounds prepared in this work, the firing temperature (chosen to give a good crystalline product for powder XRD studies),[14] the precursor metal salt and the phase composition of the fired product. The synthetic method gives an essentially quantitative yield of the metal chalcogenide. The powder XRD patterns of the fired materials were in good agreement with the literature data.[15] For the materials prepared which contain one or two phases of the same compound there is no XRD pattern evidence for the presence of crystalline impurities. Scanning electron micrographs (SEMs), presented in Fig. 1, of two of the materials prepared in this work clearly show their crystalline nature.

For cobalt, iron and copper, mixed metal oxidation state and/or nonstoichiometric sulfide phases always resulted (see Table I). This is not surprising in view of the number of nonstoichiometric sulfide phases reported for these metals,[15,16a] (determination of the exact composition of these was beyond the scope of this work). For aluminum and chromium(III) the material prepared after firing was identified as M_2O_3 (M = Al or Cr).[15] In these cases precipitates may have oxidized before firing, or may have decomposed to oxides during firing. Attempts to prepare aluminum sulfide by dissolving the metal precursor in dry polar organic solvents (such as alcohols, dimethylformamide and dimethylsulfoxide, but not reducible solvents, which would react with hydrazine) under anerobic conditions using a hydrazine monohydrate/sulfur solution also resulted in the formation of aluminum oxide on firing.

The mixed metal sulfide ZnCdS and the sulfoselenide ZnSSe formed single-phase materials. The powder XRD pattern of $Zn(S,Se)_1$ is typical of the cubic phase; the cell size of 5.54 Å is evidence that the formula of the material is approximately $Zn(S_{0.4}{\cdot}Se_{0.6})$. [17] X-ray fluorescence (XRF) analysis and comparison with standard samples gave the precise formula as $ZnS_{0.47}Se_{0.53}$. Since the chalcogen solution contained equimolar quantities of S and Se this indicates that to achieve the desired S to Se ratio, in the fired product, an excess of sulfur must be used in the parent hydrazine solution. The powder XRD pattern of $(Zn,Cd)_1S$ is typical of a hexagonal cell. The cell size was calculated to be $a = 3.98$ Å and $c = 6.49$ Å which is evidence that the approximate Zn to Cd ratio was $(Zn_{0.6}{\cdot}Cd_{0.4})S$. [18] XRF analysis and comparison with standard samples gave the precise formula as $Zn_{0.68}Cd_{0.32}S$. This suggests that, to prepare material of a given Zn to Cd ratio, a slight excess of cadmium should be used.

Electronic absorption spectroscopic studies of the reduction of sulfur by hydrazine hydrate to investigate the nature of the species

Table I. Metal sulfide and selenide materials prepared using solutions of sulfur and/or selenium in hydrazine monohydrate.

Material	Color	Comment and ICPDS pattern number[14]	Firing temperature (°C)	Starting metal salt
MnS	Green	α phase 6-0158	800	$Mn(OOCCH_3)_2$
MnSe	Brown	Cubic 11-683	800	$Mn(OOCCH_3)_2$
Fe	Black	Mixed phase of $Fe_{1-x}S$	800	$Fe(SO_4)$
Co	Brown	Mixed phases of cobalt sulfides	700	$Co(OOCCH_3)_3$
NiS	Gold	Hexagonal 2-1280	800	$Ni(SO_4)$
Cu_2S	Blue / black	Mixed phases of copper(I) sulfides	800	$Cu(OOCCH_3)_2$
ZnS	White	α and β phases, 36-1450 and 5-556	800	$Zn(OOCCH_3)_2$
$ZnS_{0.47}Se_{0.53}$	Tan	Cubic, $a = 5.56$ Å.	800	Zn(OOCCH3)2
$Zn_{0.68}Cd_{0.32}S$	Orange	Hexagonal, $a = 3.98$ Å, $c = 6.49$ Å.	900	1:1, $Zn(OOCCH_3)_2$:$Cd(OOCCH_3)_2$
ZnSe	Yellow	Cubic 15-105	800	$Zn(OOCCH_3)_2$
CdS	Yellow	Greenocktite 6-0314	800	$Cd(OOCCH_3)_2$
In_2S_3	Red	Orthorhombic 25-390	700	$In_2(SO_4)_3$
SnS_2	Orange	Hexagonal 23-677	570	$SnCl_4$
PbS	Silver	Galena *syn* 5-592	800	PbO/CH_3COOH

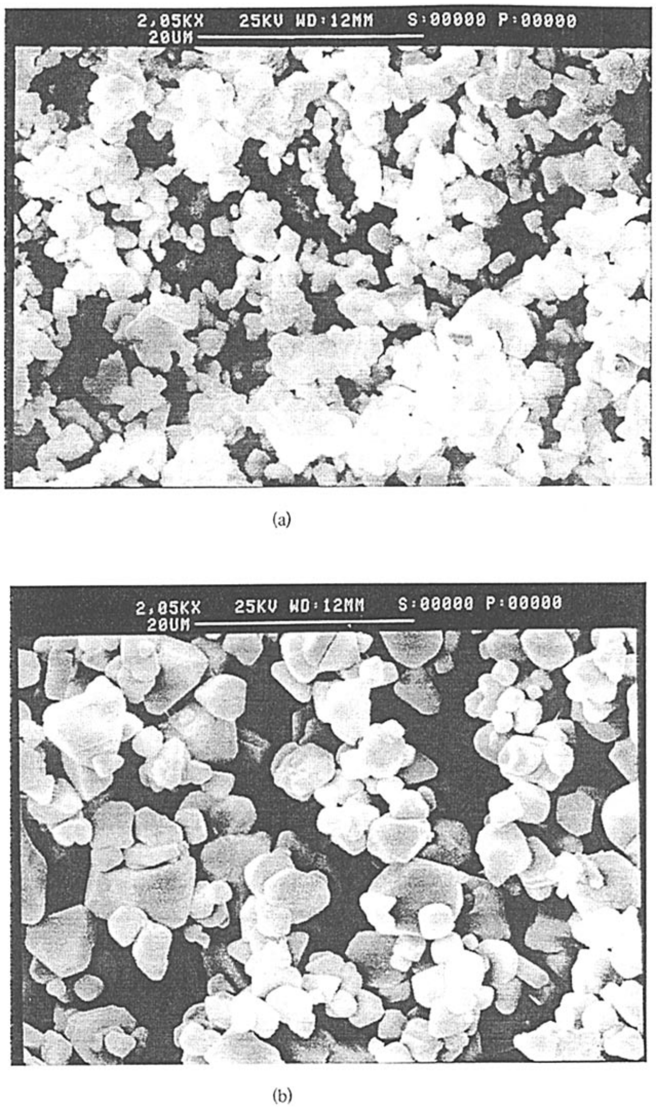

Figure 1. SEMs of (a) ZnS:Cu and (b) ZnS:Cu,Al,Au.

formed.—Hydrazine has been previously used in the reduction of metal sulfites,[6b] and in a quantitative test for selenium,[19] but until our recent work there had been no report on the preparation of metal sulfides and selenides using chalcogenide solutions in hydrazine monohydrate.[11] Sulfur-containing solutions are well established and may be formed by either dissolving the element in a suitable solvent, or by reacting a suitable solvent with the element to form soluble species.[16b] Sulfur solutions in dimethylformamide,[16b,20] aqueous base,[20,21] and molten alkali metal halide,[22] are blue in color.

Hydrazine monohydrate is a strongly reducing transparent liquid.[13] The addition of sulfur to this liquid results both in the evolution of a clear gas (not H_2S or acidic but N_2, as shown later) and the formation of an orange colored solution which turns red/brown on further addition of sulfur.[13] The decomposition products of these solutions are known to be hydrogen sulfide, ammonia, and nitrogen.[13] Polarographic studies of sulfur and selenium solutions in hydrazine hydrate have led to the suggestion that they contain polysulfide or polyselenide ions (S_n^{2-} or Se_n^{2-}).[23] Electronic absorption spectroscopic studies of electrochemically reduced sulfur solutions in dimethylformamide (which are blue) show the presence of an absorption band at 618 nm, that has been ascribed to the hexasulfide ion (S_6^{2-}).[20a] Other species which exist in equilibrium with this one are the tetrasulfide (S_4^{2-}) and the octasulfide (S_8^{2-}) these have associated electronic absorption bands at 435 and 505 nm, respectively.[20a] The strong blue color of the solution arises from a combination of all three absorption bands (with that of the S_6^{2-} being dominant).[20a]

In Fig. 2 the spectrum (a) of a low concentration (compared to the concentration used to precipitate metal sulfides) of sulfur in hydrazine monohydrate is presented. Comparison of this spectrum with those of electrochemically reduced sulfur in dimethylformamide,[20a] provides evidence for the presence of polysulfide anions, and it can be seen that the concentration of S_6^{2-} is very low (little absorbance fron 600 to 650 nm) compared to that of S_4^{2-} (400 to 450 nm). Progressively increasing the sulfur concentration causes the solution to darken through red to a dull red/brown color. Initially this is due to an increase in the absorption around 400 nm attributed to the S_4^{2-} ion concentration. However the intensity of the electronic absorption bands of more concentrated solutions is extremely high (due to the high extinction coefficient of the species in solution). Accurate measurement is impossible as the minimum extinction coefficient $= 9.94 \times 10^4$ (calculated from sulfur in hydrazine hydrate assuming all S_8 has been converted to S_4^{2-}). Hence the precise nature of the polysulfide species present in concentrated solutions remain unknown.

Electronic absorption spectra of the polysulfide ions, formed in DMF, by the reduction of sulfur by hydrazine at much lower concentrations (Fig. 2b–d) were recorded for comparison with those of electrochemically reduced sulfur (initial hydrazine concentration 5.13 mol dm^{-3}, initial sulfur concentrations shown 4.9, 7.3, and 9.7 mmol dm^{-3}). These spectra show that S_4^{2-} (400–450 nm)and S_6^{2-} (600–650 nm) species are present in the solution. The relative areas of the absorption bands show that the S_4^{2-} ion's absorption band is now dominant.

From these findings we suggest that S_4^{2-} is in the highest concentration in the solution, which appears dull brown in color, and is of the same appearance as the solutions used for material preparation in this work.

Discussion of the precipitation of metal sulfides using sulfur solutions in hydrazine hydrate.—Hydrazine is a well-known reducing agent. Previous studies have shown that the products of the reaction of hydrazine with an oxidant are affected by the pH of the solution, equations for both acidic and basic conditions are given in Fig. 3.[4b] Dissolution of sulfur into hydrazine to form polysulfide ions will occur according to the reaction given in Fig. 3 for basic conditions (since hydrazine monohydrate is strongly basic).

The addition of the hydrazine/sulfur solution to that of the metal (which results in the polysulfide ions being in a much more acidic environment and in intimate contact with the metal cations) causes immediate precipitation of the metal sulfide. Measuring the pH of the solution during the hydrazine/sulfur addition yielded the results

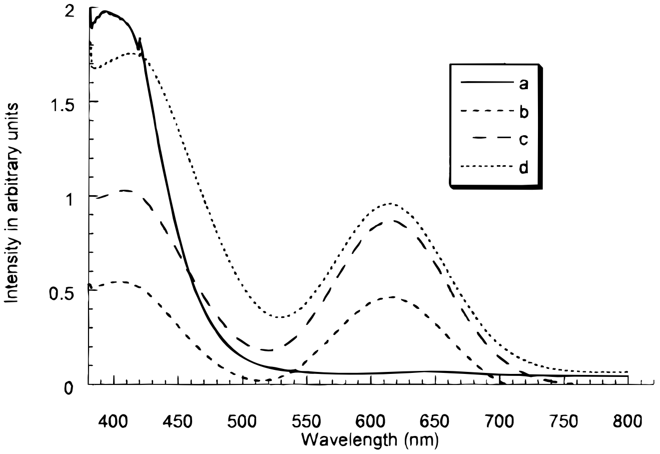

Figure 2. Electronic absorption spectra of (a) 1 mol dm^{-3} sulfur in hydrazine monohydrate; (b) 4.9 mmol dm^{-3}, (c) 7.3 mmol dm^{-3}, (d) 9.7 mmol dm^{-3} sulfur in hydrazine monohydrate (5.13 mol dm^{-3})/dimethylformamide.

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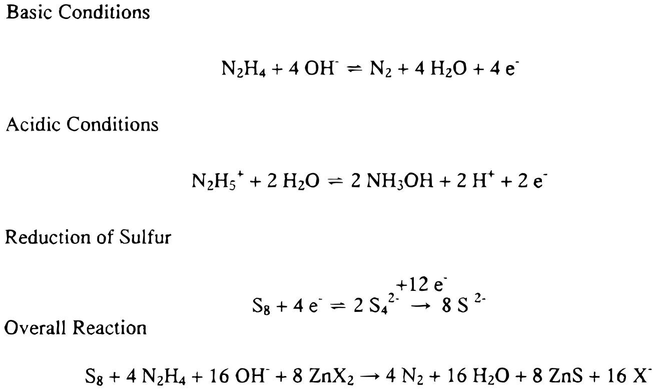

Basic Conditions

$$N_2H_4 + 4\,OH^- \rightleftharpoons N_2 + 4\,H_2O + 4\,e^-$$

Acidic Conditions

$$N_2H_5^+ + 2\,H_2O \rightleftharpoons 2\,NH_3OH + 2\,H^+ + 2\,e^-$$

Reduction of Sulfur

$$S_8 + 4\,e^- \rightleftharpoons 2\,S_4^{2-} \xrightarrow{+12\,e^-} 8\,S^{2-}$$

Overall Reaction

$$S_8 + 4\,N_2H_4 + 16\,OH^- + 8\,ZnX_2 \rightarrow 4\,N_2 + 16\,H_2O + 8\,ZnS + 16\,X^-$$

Figure 3. Reactions involved in the preparation of metal sulfides using sulfur solutions in hydrazine monohydrate.

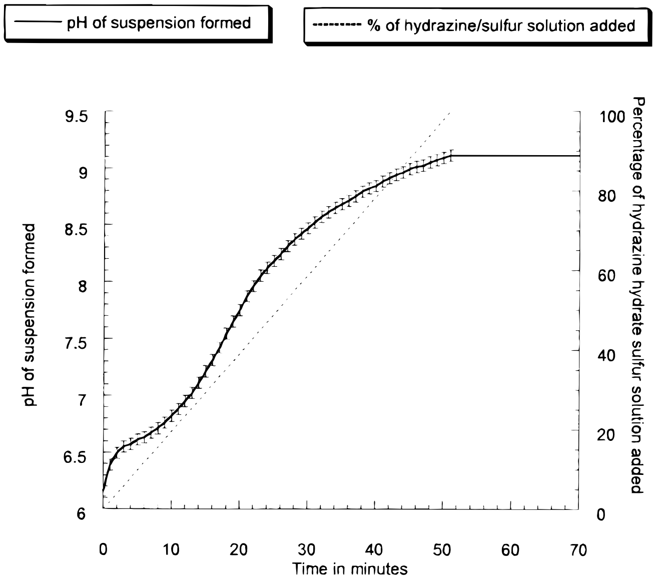

Figure 4. Variation of the pH of a zinc salt solution during the addition of a sulfur solution in hydrazine monohydrate.

shown in Fig. 4. It can be seen that for 400 mL of 0.5 M ZnOAc solution, the pH starts in the acidic region but becomes progressively more basic on the addition of the hydrazine sulfur solution. This is not surprising in view of the excess hydrazine used in these solutions. We suggest that this is not evidence that both reactions, shown in Fig. 3, occur as the precipitation is so fast that it takes place in localized basic areas before homogeneous mixing has been achieved. This can be inferred as no tendency for the alkalinity of the solution to decrease was seen on standing after homogeneous mixing had been achieved. If discernible quantities of hydrazine were still reducing sulfur a lowering of the pH would have been observed.

X-ray powder diffraction studies of the unfired zinc sulfide precipitates confirmed the presence of small amounts of sulfur as an impurity. The crystalline elemental sulfur is seen clearly in the powder diffraction pattern as are broad X-ray peaks arising from semicrystalline unfired zinc sulfide. Soxhlet extraction with carbon tetrachloride was used to measure the amount of sulfur in the precipitate. This was almost exactly the excess of sulfur used in the reaction, and accounted for the excess yield over the theoretical maximum. This confirms that the unfired precipitate is zinc sulfide and indicates that the polysulfide ions have been reduced to sulfide ions in the reaction vessel. The excess sulfur used reverts to S_8 under nonreducing conditions, explaining the observation of S_8 in the powder XRD pattern.

A working, balanced overall reaction is presented in Fig. 3. A more complete reaction scheme truly describing the reaction in full is impossible to write until all the polysulfides and their concentrations in the hydrazine hydrate solution are known, and such a study is beyond the scope of this work. However we have shown that the dissolution of sulfur in hydrazine monohydrate results in the formation of a range of polysulfide ions, including predominently tetrasulfide and some hexasulfides. When the polysulfide solution is added to a metal salt solution the precipitation of metal sulfide occurs.

Preparation of metal sulfide and selenide phosphors.—We have previously demonstrated that this method is useful for the preparation of ZnS:Ag phosphors with high emission efficiencies.[11] However the emission spectra have a slightly more red-shifted wavelength than commercial phosphors and initially manifested a tail into the green region of the spectra which is not present in the emission spectra of a commercial material.[11] Such a tail is caused by the presence of oxidation products of zinc sulfide, formed during the firing process. Tight packing of the unfired materials into a silica crucible, and rigorous washing with acetic or sulfurous acid after firing have been used to remove this tail from the emission spectra.[1] The red-shifted emission spectra (compared to that of the commercial material) resulted in a ZnS:Ag with CIE *y* coordinate considerably larger than that of the commercial material (see Table II). The effect of the initial pH of the zinc salt solution, before addition of the sulfur solution, on the properties of the final phosphor were examined over the range pH 1–6. No visible effects on particle morphology or particle size were found (see Table II), and the samples phase composition (containing both cubic and hexagonal ZnS)[15] was also unaffected. Constant current cathodoluminescent emission testing revealed no

Table II. Particle sizes and CIE coordinates for (ZnS:Ag) phosphors.

(ZnS:Ag)	Mean diam (μm)	SD (μm)	Dominant (λ/nm)	CIE-*x*	CIE-*y*
Previous work	7.640	4.71	475.07	0.1704	0.1466
Commercial	6.383	2.87	465.21	0.1499	0.0574
Aqueous HCl pH 1 [a]	5.413	4.52	472.95	0.1578	0.1120
Aqueous HCl pH 2 [a]	5.141	3.71	472.54	0.1592	0.1117
Aqueous HCl pH 3 [a]	5.072	4.44	472.15	0.1577	0.1121
Aqueous HCl pH 4 [a]	5.098	4.82	473.05	0.1584	0.1118
Aqueous HCl pH 5 [a]	5.204	4.61	472.67	0.1597	0.1124
Aqueous HCl pH 6 [a]	5.342	3.98	472.09	0.1595	0.1118
Water [a]	5.049	3.44	472.04	0.1593	0.1113
Methanol [a]	4.531	3.31	465.12	0.1745	0.0819
Ethanol [a]	5.212	4.28	462.00	0.1563	0.0666
Propan-2-ol [a]	5.354	3.31	466.35	0.1480	0.0604
Butan-2-ol [a]	5.354	6.92	462.66	0.1554	0.0545

[a] Solvent from which the unfired ZnS was precipitated.

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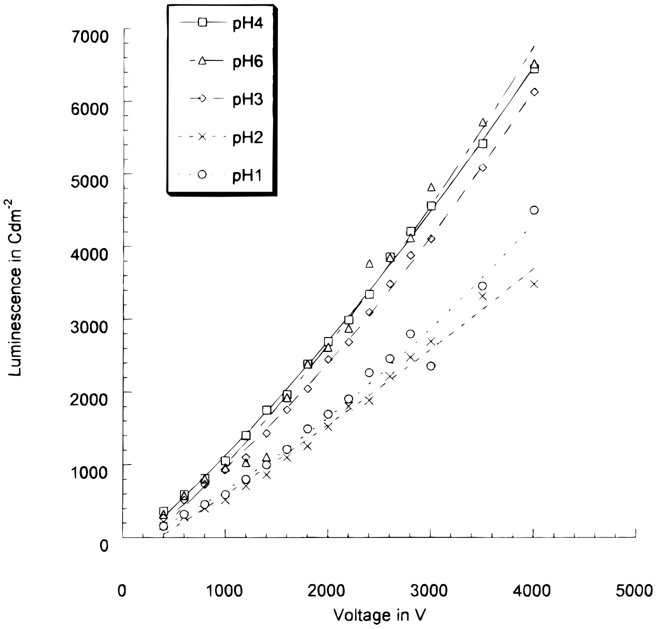

Figure 5. Constant current CL emission intensity against voltage for ZnS:Ag phosphors precipitated from various pH solutions.

discernible variation in the chromaticity of the blue emission of the phosphors, and that the CIE coordinates were not improved with respect to those of the commercial material (see Table II). The plot of the emission intensity against voltage, presented in Fig. 5, does, however, reveal evidence of a decreased emission intensity for the samples which were prepared from the more acidic solutions. From this we infer that suitable zinc salts which form less acidic solutions are the favored starting materials. In an attempt to produce materials with CIE coordinates comparable to commercial ZnS:Ag the effect of the solvent in which the zinc and silver salts were dissolved was examined. The alcohols used were methanol, ethanol, propan-2-ol, and butan-2-ol.

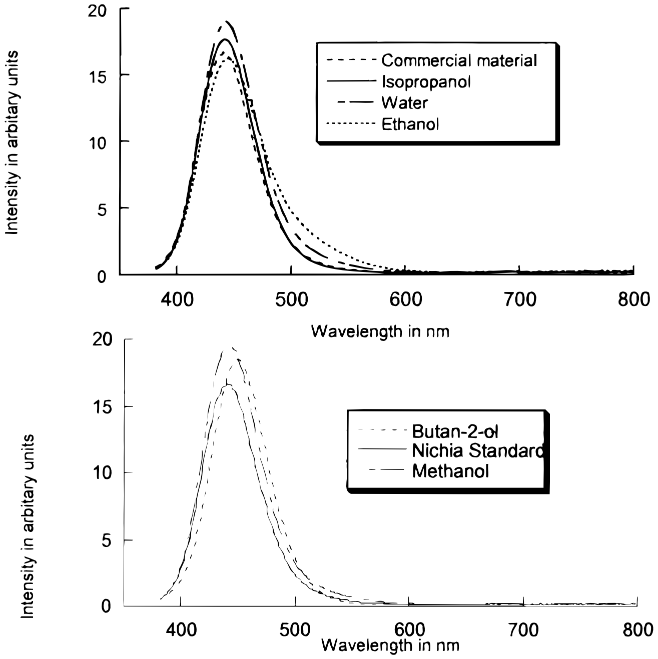

Figure 6. CL emission spectra of ZnS:Ag phosphors precipitated from organic alcohols.

Alcohols were used in place of water as they are suitable solvents in which to dissolve metal salts, and they are not reduced by hydrazine monohydrate (reducible solvents, such as ketones, are totally unsuited to this method as they react with the hydrazine). Scanning electron micrographs (SEM) and Coulter counter particle size measurement provide evidence that the particle size and distribution of all the fired materials were similar to those of the commercial material. The commercial sample contains predominately cubic ZnS (with a minor hexagonal component). The powder XRD patterns of samples prepared from a range of alcohols in this work showed that they contained both cubic and hexagonal phases. It appears that the solvent from which the ZnS is precipitated has no discernible effect on the phase composition or particle size of the final material. The CL emission spectra and a plot of constant current emission intensity against voltage for the materials precipitated from various alcohols are shown in Fig. 6 and 7, respectively. Table II presents the CIE coordinates and particle sizes of both our materials and and commercial ZnS:Ag materials. It can be seen that the effect of the solvent is to reduce the dominant wavelength when the longer chain alcohols are used. From this observation it appears that it is possible to control the chromaticity of the emission spectrum by changing the solvent in which the metal salt solution is prepared. The most saturated blue emission from ZnS:Ag is obtained by precipitating the material from butan-2-ol. In addition, careful selection of the solvent, facilitates the preparation of ZnS:Ag phosphors manifesting higher efficiencies in the 0-5000 V range, with comparable particle sizes, and CIE coordinates (under CL excitation) to commercial material.

In parallel studies samples of ZnS:Cu, ZnS:Cu,Al, ZnS:Cu,Al,Au, Zn(S,Se):Cu, and (Zn,Cd)S:Cu have been prepared to confirm the general application of this method for the preparation of group II-VI phosphors. In the preparation of ZnS:Cu materials and related systems no significant difference between the chromaticity of the materials prepared from an aqueous solution using a sulfur solution in hydrazine monohydrate to those of commercial materials was found. The chromaticity and emission spectra of the ZnS:Cu phosphor prepared are in excellent agreement with those of the commercial material (presented in Fig. 8 and Table III) while the intensity of the constant current CL emission is significantly better than that of the commercial sample used over the voltage range examined (0-4000 V) (see Fig. 9).

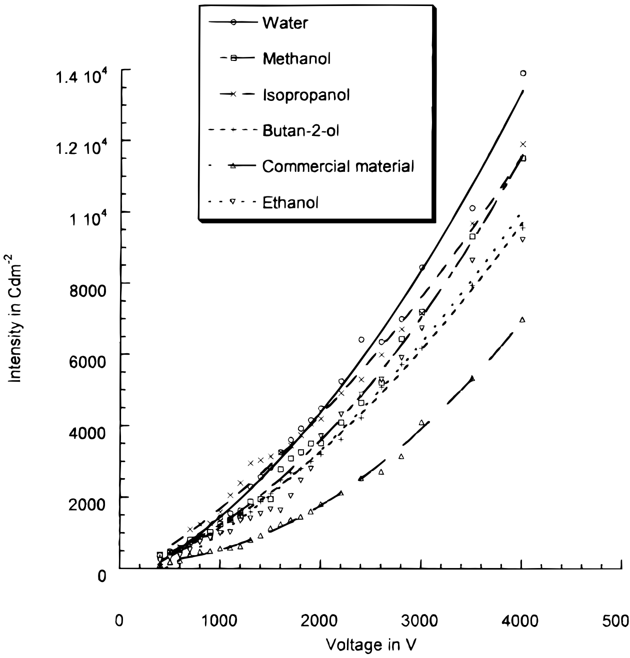

Figure 7. Constant current CL emission intensity against voltage for ZnS:Ag phosphors precipitated from organic alcohols.

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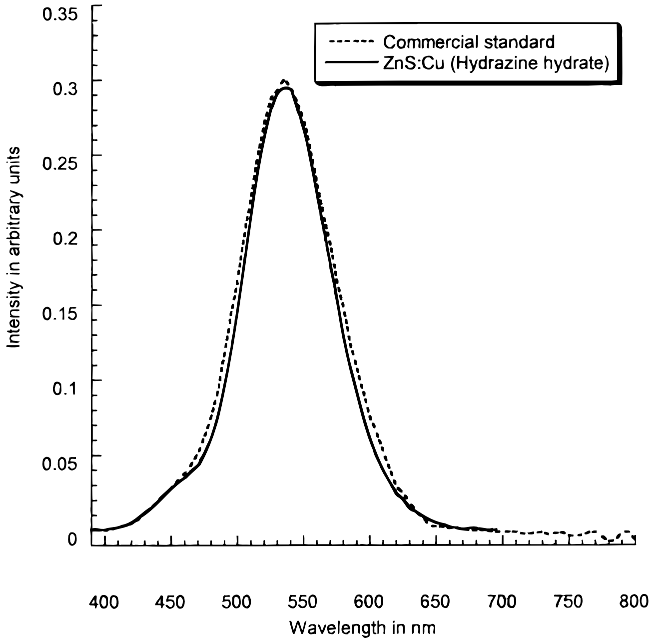

Figure 8. CL emission spectra of ZnS:Cu phosphors.

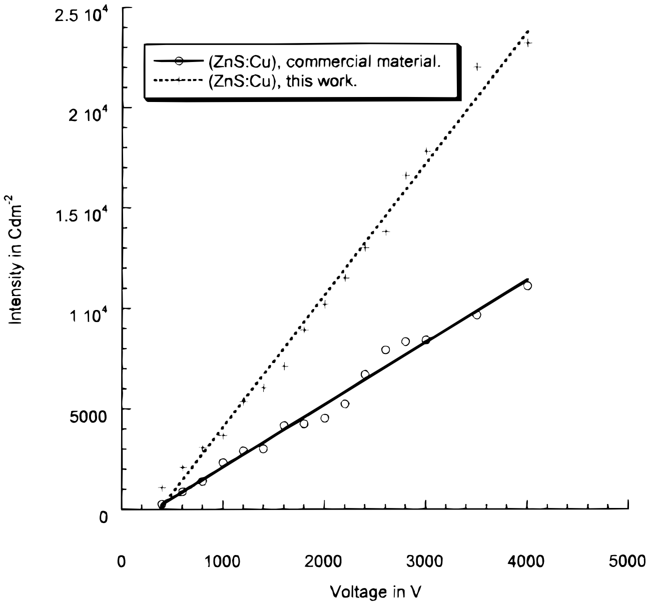

Figure 9. Constant current CL emission intensity against voltage for ZnS:Cu phosphors.

ZnS:Cu,Al and ZnS:Cu,Al,Au phosphors were prepared from aqueous solutions of metal salts using the standard method. Table III lists the chromaticity and particle sizes of the materials, and Fig. 10 presents the CL emission spectra of the materials. The CL emission spectra of the materials prepared in this work have a shoulder at low wavelengths not present in the commercial material. This shoulder alters the chromaticity of the materials, but the maxima of the main peaks are in good agreement with those of the commercial materials. It is probable that the shoulder is caused by a slight deficiency in the desired copper content, similar shoulders are observed in ZnS:Cu with decreasing copper concentration.[2c] The constant current CL emission intensity plotted against voltage is given in Fig. 11; it reveals these materials are less efficient than the commercial materials. The study of the precipitation of aluminum salts using this method as discussed earlier showed that it was unsuitable for the preparation of Al_2S_3. Aluminum is added to alter the chromaticity of the ZnS:Cu, however, it reduces the efficiency of the material.[2c] This suggests that incomplete precipitation of the aluminum from the stock solution is not the cause of the low efficiency of the materials and therefore backs up the hypothesis that the copper concentration is lower than ideal.

Table III. Particle sizes and CIE coordinates for (ZnS:Cu) phosphors and related materials.

Phosphor	Mean diam (μm)	SD (μm)	Dominant (λ/nm)	CIE-*x*[a]	CIE-*y*[a]
(ZnS:Cu) This work	8.458	8.55	546.25	0.2863	0.5494
(ZnS:Cu) Commercial	4.731	4.65	547.23	0.2983	0.5615
(ZnS:Cu,Al) This work	9.218	5.46	536.81	0.2698	0.5424
(ZnS:Cu,Al) Commercial	6.080	6.22	550.99	0.3087	0.6108
(ZnS:Cu,Al,Au) This work	7.355	3.36	542.77	0.2996	0.6094
(ZnS:Cu,Al,Au) Commerical	8.273	7.97	549.11	0.2819	0.5655
({Zn,Cd}1S:Cu) This work	4.554	1.30	595.51	0.5894	0.3962
(Zn{S,Se}1:Cu) This work	4.641	2.23	588.87	0.5572	0.4342

[a] Cathodoluminescent CIE coordinates, except for (Zn,Cd)S and Zn(S,Se) which are photoluminescent CIE coordinates.

The preparation of (Zn,Cd)S:Cu and Zn(S,Se):Cu were also carried out from aqueous solution, by the standard method. The major stoichiometries of the materials formed were simillar to those discussed earlier in this work. Both phosphors luminesced red under 366 nm UV light. Photoluminescent emission spectra were recorded and are shown in Fig. 12. Although no CL investigation of the latter phosphors was undertaken, the PL emission spectra show that the use of a sulfur and or selenium solution in hydrazine monohydrate offers a suitable method for the preparation of group II-VI phosphors other than ZnS materials.

Conclusions

We have demonstrated that a polysulfide solution is formed by the dissolution of sulfur in hydrazine monohydrate. This solution

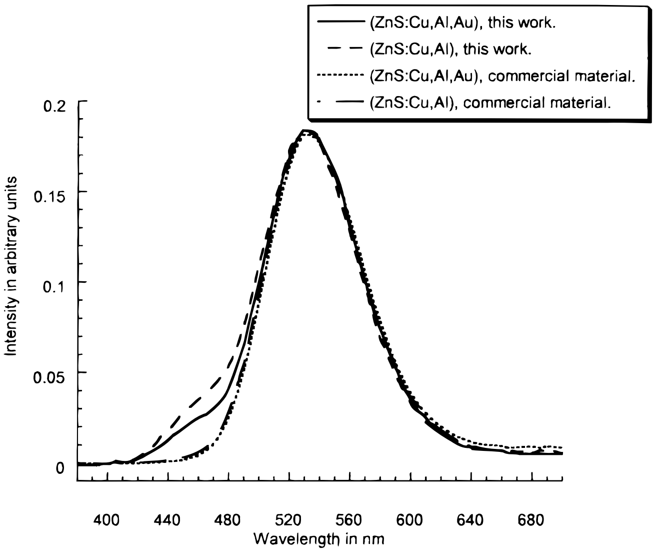

Figure 10. CL emission spectra of ZnS:Cu,Al and ZnS:Cu,Al,Au phosphors.

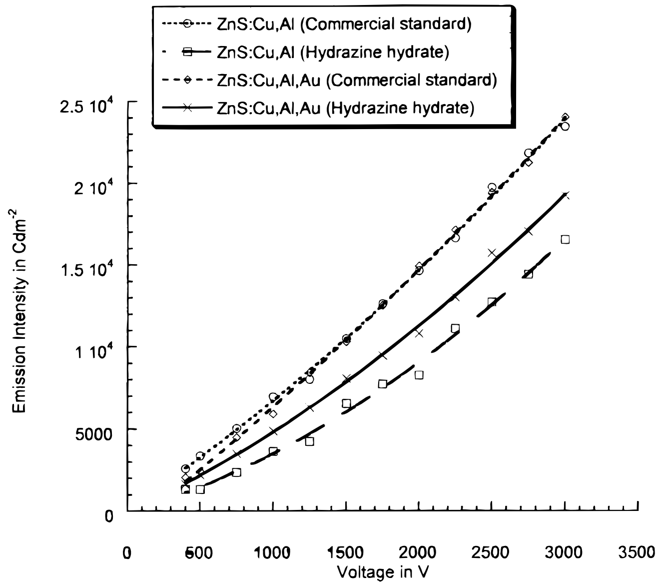

Figure 11. Constant current CL emission intensity against voltage for ZnS:Cu,Al and ZnS:Cu,Al,Au phosphors.

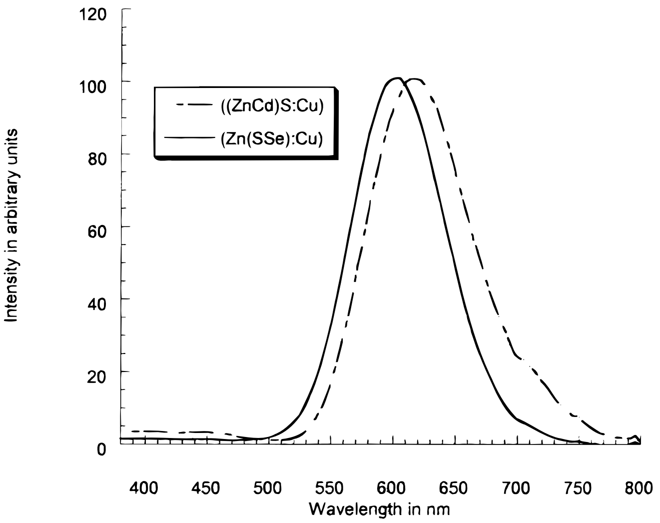

Figure 12. PL emission spectra of (ZnCd)$_1$S,Cu and Zn(SSe)$_1$:Cu phosphors.

can be used to precipitate many metal sulfides from solution, and the precipitate, after firing, is a crystalline metal sulfide. It has also been shown that an analogous method, using selenium instead of sulfur in hydrazine monohydrate, is suitable for the preparation of metal selenides. The method is rapid and limits the amount of sulfurous waste gases formed during preparation of the metal sulfide. The range of materials that can be prepared has now been demonstrated to be much more general than previously thought. The application of this work to the synthesis of group II-VI phosphors has yielded many materials with interesting luminescent properties.

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