Preparation of Zinc Oxide and Zinc Sulfide Powders by Controlled Precipitation from Aqueous Solution

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ZnO and ZnS powders were prepared from aqueous solutions of zinc salts in the presence of ethylenediamine or triethanolamine. The morphology of the powders was analysed by scanning electron microscopy and infrared spectroscopy. The effect of the experimental conditions upon the size and shape of the particles is described with a special emphasis on the role of the organic ligand.

There is considerable current interest in developing microcrystalline powders suitable for use as precursors for ceramic materials. This work forms part of various efforts to produce high-performance ceramics of homogeneous composition and microstructure, as such materials should have improved reliability as compared to conventional materials.[1] The electrical properties of zinc oxide are also markedly affected by the characteristics of the precursors used to prepare an individual sample, these properties are crucial in defining the suitability of zinc oxide for use in varistors.[2-5] Zinc sulfide is another example of a material for which the control of particle formation may be of importance as this material is used in luminescence devices and pigments.[6]

Chemical methods have been applied to the synthesis of powdered materials, and submicrometre particles of narrow size distribution, high purity and uniform morphology have been achieved.[1,7,8] Although technological interest in such controlled synthesis is recent, many natural systems synthesize biominerals with remarkable properties.[9]

Matijevic[8] showed that well defined hydrated metal oxide particles, as well as other inorganic solids, can be precipitated from homogeneous aqueous solution by several methods including the thermal treatment of solutions of coordination complexes. The method is based on forming a complex sufficiently stable to prevent spontaneous precipitation at room temperature, i.e. masking the metal ion with a suitable ligand. Raising the temperature promotes the dissociation of the complex and allows the controlled generation of free metal ion which, on hydrolysis, leads to precipitation. Well defined particles of iron oxides,[10] nickel and cobalt both as metal or oxide[11] have been prepared by such methods. If an appropriate chalcogenide source is added, such methods can be used to prepare sulfides and selenides.[8] Needle-like crystals of ZnO were obtained by the hydrothermal decomposition of aqueous solutions of Na$_2$Zn–EDTA[12] and spherical particles of ZnO were prepared using a spray pyrolysis method.[13] The controlled preparation of ZnS particles has been achieved[14] using thioacetamide as a source of sulfide, but with no other added organic ligand.

This paper reports the synthesis and characterization of ZnO and ZnS powders by precipitation from homogeneous solution, and the effect of experimental conditions on the morphology of the products is discussed. The work is part of a programme aimed at collecting systematic information about the role of chelating agents in the control of powder morphologies which should help to underpin the mechanism initially proposed by LaMer and Dinegar[15] for the formation and shape control of colloidal particles.

Experimental

Chemicals

The following chemicals were used without further purification: zinc nitrate hexahydrate, Zn(NO$_3$)$_2$·6H$_2$O (Merck); zinc sulfate heptahydrate, ZnSO$_4$·7H$_2$O (Merck); zinc chloride, ZnCl$_2$ (Merck); zinc acetate dihydrate, Zn(CH$_3$CO$_2$)$_2$·2H$_2$O (Merck); sodium hydroxide, NaOH pellets (Pronalab); nitric acid 65%, HNO$_3$ (Merck); sodium chloride, NaCl (Merck); sodium nitrate, NaNO$_3$ (Merck); sodium sulfate decahydrate, Na$_2$SO$_4$·10H$_2$O (Merck); sodium acetate, NaCH$_3$CO$_2$ (Merck); ammonia, NH$_3$ (Merck); ethanolamine, NH$_2$CH$_2$CH$_2$OH, (Merck); triethanolamine (tea), N(CH$_2$CH$_2$OH)$_3$ (Merck); diethylamine, NH(CH$_2$CH$_3$)$_2$ (Merck); ethylenediamine (en), NH$_2$CH$_2$CH$_2$NH$_2$ (Merck); diethylenetriamine (dien), NH(CH$_2$CH$_2$NH$_2$)$_2$ (BDH); triethylenetetramine (trien), NH$_2$CH$_2$CH$_2$NHCH$_2$CH$_2$NH-

Table 1 Experimental conditions for the preparation of ZnO samples using zinc nitrate at pH 13.0

sample	aging temp./°C	aging time/min	organic ligand
A	150	120	en
B	150	120	tea
C	100	120	en
D	100	120	tea
E	100	120	—

Table 2 Experimental parameters used in the prepartion of ZnO powders

ligand	pH (20 °C)	anion^a	time/min	T/°C	I(NaNO$_3$)/mol kg^{-1}
tea	10.0	NO$_3^-$	5	70	0.31
en	11.0	SO$_4^{2-}$	30	80	0.56
—	12.0	Cl$^-$	60	90	0.81
—	13.0	CH$_3$CO$_2^-$	120	100	1.06
—	—	—	240	150^b	not controlled

^{a} The respective zinc salt was used and an excess of the sodium salt (0.025 or 0.05 mol) was added to 50 cm^3 of solution. ^{b} Hydrothermal conditions.

Table 3 Results from precipitation experiments of aqueous solutions of zinc nitrate and organic ligands at room temperature and pH 12.0

ligand[a]	solid
ammonia	zinc hydroxide
diethylamine	zinc hydroxide
monoethanolamine	zinc hydroxide
triethanolamine	none
ethylenediamine	none
diethylenetriamine	none
triethylenetetramine	none
nitrilotriacetic acid	none
EDTA	none

[a] $[Zn^{2+}] = 0.02$ mol dm^{-3}; [ligand]:[Zn^{2+}] = 5:1.

Table 4 Results from precipitation experiments of aqueous solutions of zinc nitrate and organic ligands at 100 and 150 °C, aging time 2 h and pH 12.0

ligand[a]	solid
triethanolamine	ZnO
ethylenediamine	ZnO
diethylenetriamine	none
triethylenetetramine	none
nitrilotriacetic acid	none
EDTA	none

[a] $[Zn^{2+}] = 0.02$ mol dm^{-3}; [ligand]:[Zn^{2+}] = 5:1.
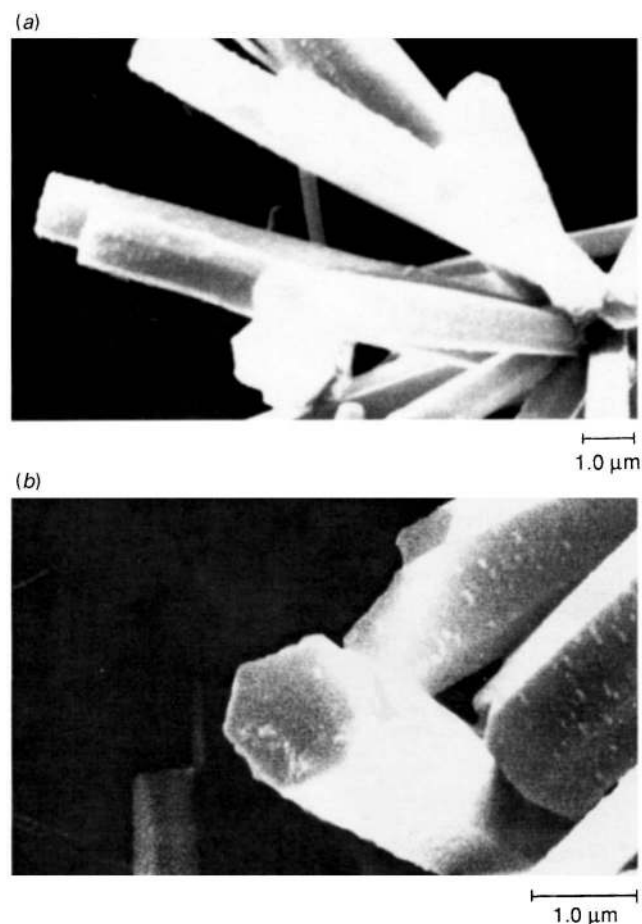
Fig. 1 SEM images of ZnO obtained by the hydrothermal treatment (150 °C) in the presence of: (a) ethylenediamine; (b) triethanolamine
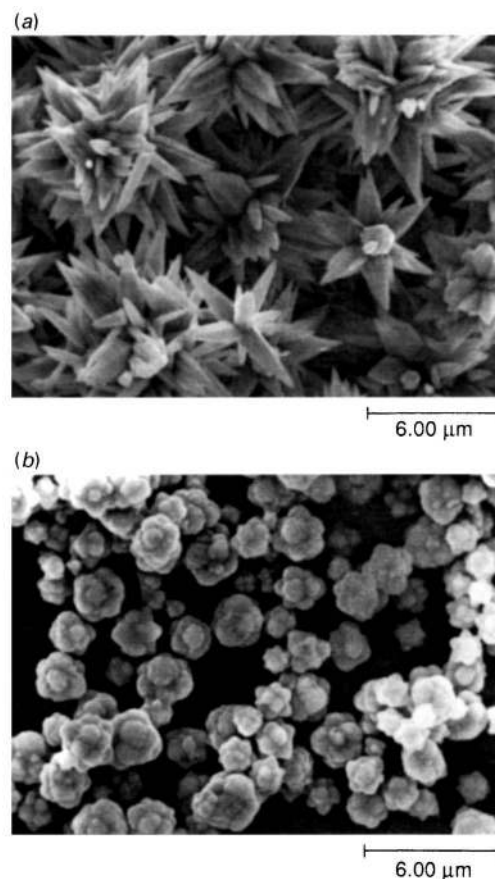
Fig. 2 SEM images of ZnO obtained at 100 °C in the presence of (a) ethylenediamine; (b) triethanolamine

CH$_2$CH$_2$ (Riedel-de-Haën); EDTA, (HO$_2$CCH$_2$)$_2$-NCH$_2$CH$_2$N(CH$_2$CO$_2$H)$_2$ (Carlo Erba); nitrilotriacetic acid trisodium salt, N(CH$_2$COONa)$_3$ (ICN); 2-mercaptoethanol, HSCH$_2$CH$_2$OH (Merck); o-phthaldialdehyde. C$_6$H$_4$(CHO)$_2$ (BDH); thioacetamide, CH$_3$CSNH$_2$ (Merck).

Sodium hydroxide solutions were prepared (1 and 4 mol dm^{-3}) using boiled deionized water. Nitric acid solutions of the same molarity were prepared by dilution of the concentrated acid. Stock aqueous solutions of zinc (0.04 mol dm^{-3}) and ligand (0.2 mol dm^{-3}) were prepared. All the solutions were filtered using 0.45 μm Millipore membranes before use.

Determination of en was performed by the colorimetric method described by Hihara et al.[16] using a Varian DMS 300 spectrometer. The stock solutions were diluted 1000-fold for the determination.

Particle Preparation

In a typical screening procedure equal volumes of ligand and Zn^{II} stock solutions were mixed and the pH adjusted to 12.0. The final mixture was left to stand with stirring, at room temperature, for at least 1 day. Thermal treatment of the solutions was performed only for those which did not give a spontaneous precipitate at room temperature. Heating procedures included refluxing (e.g. for 2 h) or heating the solutions in PTFE reaction bombs, in an oven (e.g. 2 h at 150 °C).

Another procedure involved the addition of sodium hydroxide (4 mol dm^{-3}) to a solution of the zinc salt (0.02 mol dm^{-3}). Initially a precipitate formed which dissolved at pH > 13.5. This solution was filtered and then refluxed; a precipitate then formed. The precipitates formed by both procedures were removed by filtration with 0.45 μm Millipore
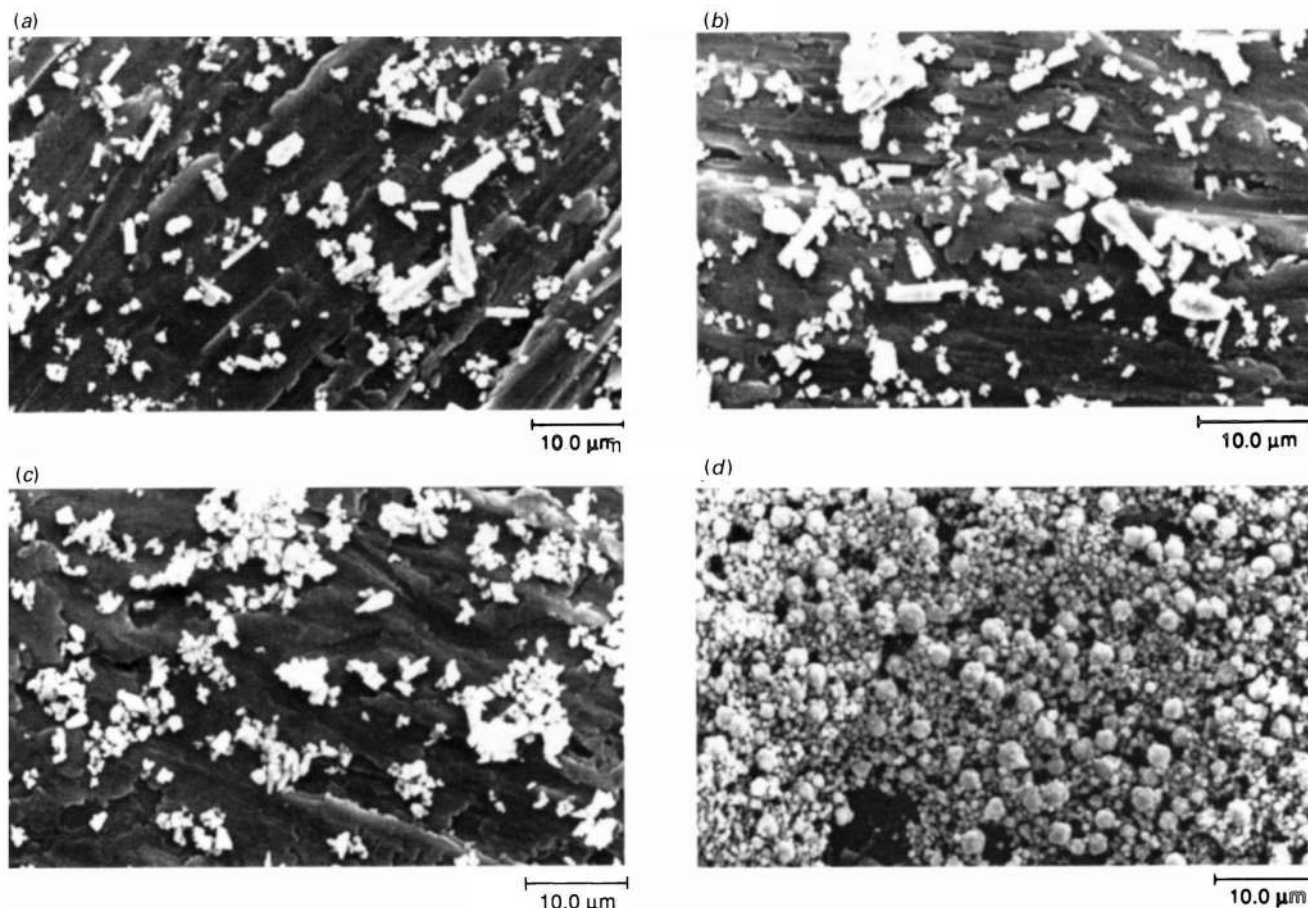
(a)

(b)

(c)

(d)

Fig. 3 SEM images of ZnO after the milling of the powders: (a) sample A; (b) sample B; (c) sample C; and (d) sample D
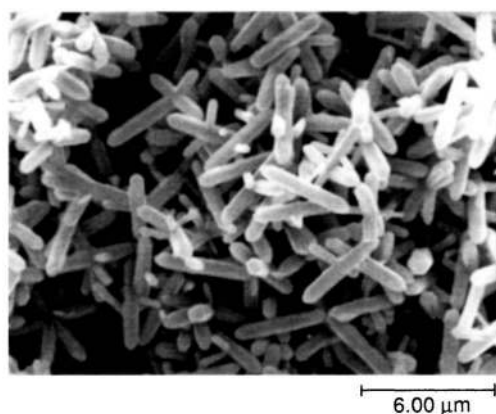

Fig. 4 SEM image of ZnO obtained at 100 °C in the absence of organic ligand

membranes, washed with deionized water and dried in a desiccator over silica gel at room temperature.

The various powders obtained were analysed (see Table 1 for sample identification). The effect of other experimental parameters associated with the preparation of the ZnO powders was studied by systematically varying the reaction conditions (see Table 2).

ZnS powders were prepared using procedures similar to those used in the preparation of ZnO. Thioacetamide was used to generate the sulfide ions.

Particle Characterization

The X-ray analysis of the powders was performed using a Philips PW 1729 generator using nickel-filtered Cu-Kα radiation. JEOL JSM-35C and Hitachi S-4100 scanning electron microscopes were used. The materials were prepared for microscopy by resuspension in water followed by ultra-sonication. Aliquots of the suspensions were then kept on high-purity aluminium rods at room temperature in a desiccator over calcium chloride until the liquid had evaporated. The infrared spectra were recorded with a Mattson Polaris FTIR spectrometer using pellets of 1 mg of the sample and 150 mg of spectroscopic-grade KBr.

Results and Discussion

Preparation of ZnO and ZnS Powders

Preliminary studies of the thermal and hydrothermal treatment of aqueous solutions of zinc in the presence of a wide variety of ligands have been reported.[17] The results of these studies suggest that en and tea are the most promising metal-ion buffers for a detailed study.

Using similar systems but with different experimental conditions Matijevic and co-workers have obtained[13,19] ZnO particles with morphological characteristics similar to those described in our preliminary report.[17] However, in the present paper the influence of a wider range of experimental conditions on the powder characteristics are reported.

The addition of an organic ligand to a solution of a zinc salt may prevent or inhibit the precipitation of zinc hydroxide.
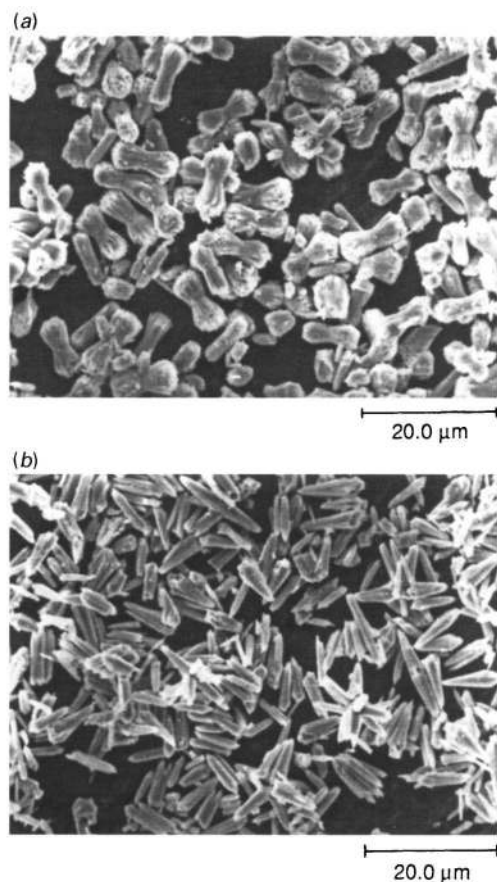
Fig. 5 SEM images of ZnO prepared (a) in the presence of an excess of sulfate ions and ethylenediamine and (b) from a solution with an ionic strength of 1.06 mol kg^{-1} and in the presence of ethylenediamine
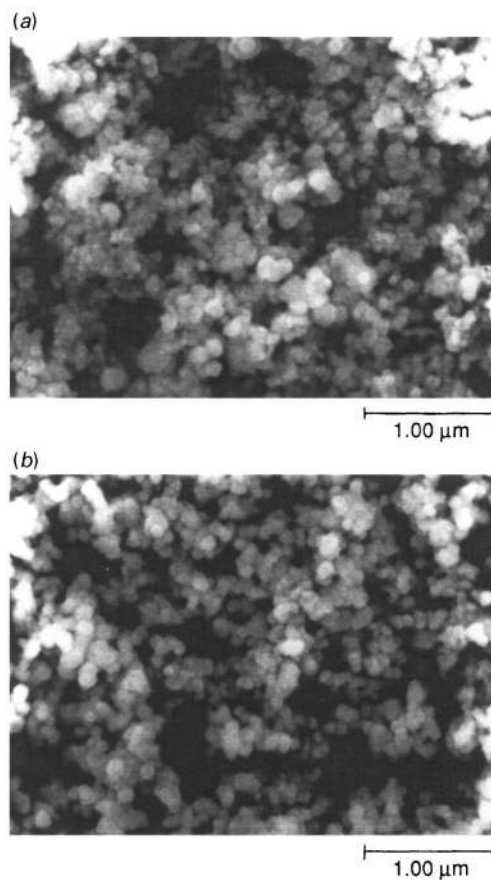

Fig. 6 SEM images of ZnS prepared at 60 °C for 2 h from solutions containing thioacetamide and (a) ethylenediamine or (b) triethanolamine

In order to select ligands which prevent the spontaneous, immediate formation of solid, precipitate-screening experiments were carried out as described in the Experimental section. The results of these studies (all carried out at room temperature) are summarized in Table 3 for a [ligand]: [Zn^{2+}] ratio of 5:1. The presence of the amines, aminopolycarboxylic acids and tea prevents the precipitation of the solid at room temperature and these ligands were chosen for more detailed investigation.

The white precipitates obtained from the solutions at room temperature exhibit very poorly defined X-ray diffraction patterns with no well defined peaks, the material formed being X-ray amorphous. The composition of the samples was confirmed as hydrated zinc oxide by comparing their infrared spectra with that of the precipitate obtained by mixing solutions of sodium hydroxide and zinc nitrate.

Zinc oxide was observed to precipitate after solutions containing tea or en were heated at pH 12.0–13.0. Hydrated zinc hydroxide precipitate is unstable at temperatures > 35 °C with respect to ZnO, in alkaline solution[20] and at high pH the formation of the oxide is expected. Ligands other than ethylenediamine or triethanolamine totally inhibited precipitation under the conditions studied, even using higher aging temperatures, see Table 4.

There appears to be only one report in the literature[14] of the preparation of ZnS particles of uniform morphology by the thermal decomposition of solutions of thioacetamide and zinc. The procedure reported involved a two-step process. No added organic ligand was used, other than the thioacetamide used as the source of sulfide ion. This method[14] involved the preparation of ZnS seeds from a solution of zinc nitrate, nitric

acid and thioacetamide, which were allowed to age further at an elevated temperature. The fact that the ligands en and tea had a marked effect on the morphology of the particles led us to investigate the effect of these chelating agents on the preparation of ZnS.

When alkaline or acidic solutions of thioacetamide were heated in the presence of metal ions, metal sulfides precipitated. In a formal sense the reaction is a consequence of the hydrolysis of thioacetamide, which may be represented as:

$$CH_3CSNH_2 + 2H_2O \rightarrow CH_3CO_2NH_4 + H_2S \qquad (1)$$
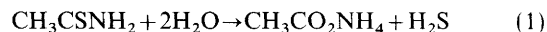
In an initial attempt to prepare ZnS particles, alkaline solutions containing the organic ligands en or tea, zinc nitrate and thioacetamide were heated at 60 or 100 °C. However, only for acidic conditions was the preparation of well defined ZnS particles successful.

Influence of Preparation Methods on Powder Characteristics

The powders obtained by thermal treatment were identified as being zinc oxide (wurtzite, hexagonal) or zinc sulfide (sphalerite, cubic). The materials were identified by comparing their diffraction patterns with published data.[21] The peaks for the zinc oxide samples were well defined, indicating that the samples were of good microcrystallinity. The best patterns were obtained for the powders prepared in closed vessels at the higher temperatures (samples A and B, Table 1). The ZnS particles were all of ill defined crystallinity, although the characteristic reflections of the cubic form could be observed.

The morphology of the particles was analysed by scanning electron microscopy (SEM). The ZnO particles obtained at

150 °C were present as twinned crystals in which the hexagonal crystal habit of the wurtzite type structure is evident (Fig. 1). These particles are similar to those obtained by other authors using hydrothermal methods.[12,18] When the reflux treatment was applied to the reaction mixtures a different morphology was observed with smaller polycrystalline particles. The effect of the ligand on the particle morphology is remarkable (Fig. 2): ZnO particles obtained in the presence of tea are nodular aggregates, but when en is used the particles are acicular. Preferential growth in the c direction has possibly occurred from a particle centre where twinning took place. When the powder samples obtained in the presence of en either from reactions at 150 °C, or from the reflux method, were mechanically milled the particles break from several sites [Fig. 3(a)–(c)]. The same milling procedure applied to samples prepared in the presence of tea by the reflux methods deaggregates the material into smaller nodular particles, some of them being broken while others remain intact [Fig. 3(d)].

In the absence of organic ligands, spontaneous precipitation may occur in alkaline solutions at room temperature. Zinc hydroxide is slightly soluble in water and becomes more soluble as the pH is increased (or lowered) above certain values. The dissolution of the precipitate is possible in a strongly alkaline medium with the formation of hydroxycomplexes such as $[Zn(OH)_3]^-$ and $[Zn(OH)_4]^{2-}$ in solution.[22] When a clear zinc solution was refluxed at pH 13.5, a powder formed (sample E), which was identified by X-ray diffraction as ZnO. SEM of this powder (Fig. 4) reveals prismatic particles of a shape and size distinctly different from those obtained in the presence of the organic ligands.
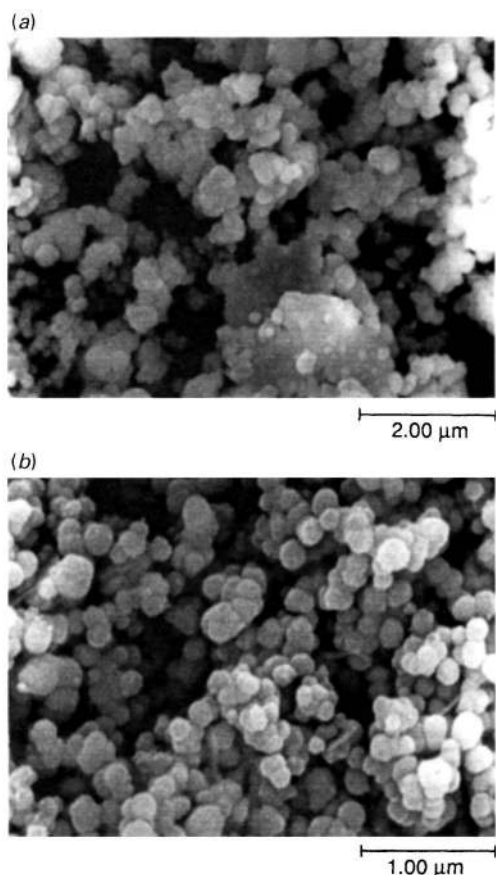
(a)

2.00 μm

(b)

1.00 μm

Fig. 7 SEM images of ZnS prepared at 100 °C for 30 min from solutions containing thioacetamide and (a) ethylenediamine or (b) triethanolamine
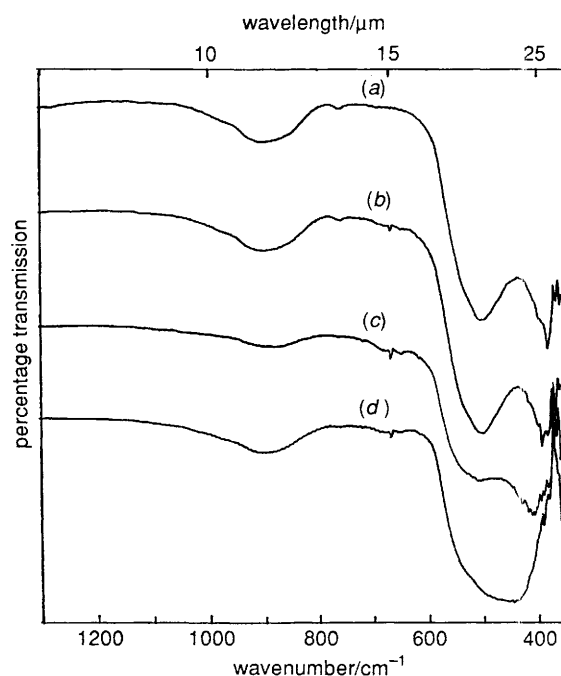

Fig. 8 FTIR spectra of the ZnO samples: (a) sample A, (b) sample B, (c) sample C and (d) sample D in KBr pellets

Some published work on the preparation of well defined particles in the presence of organic ligands has used equilibrium arguments[23] while in other cases the chemical degradation of the organic ligand has been involved.[11] In an attempt to clarify the fate of the ligand for the present systems en was quantitatively determined in the solutions from which ZnO precipitation had occurred. The results of these experiments showed that the en does not decompose.

An effort was made to determine if parameters such as pH, the anion, the reaction time, the temperature and the ionic strength affected the ZnO powders. The experimental parameters summarized in Table 2 were studied and the results showed no evidence for a pronounced effect of these variables on the characteristics of the ZnO particles, in contrast to the ligand or the nature of the hydrothermal treatment. In two cases slight effects were noticed. Slightly different ZnO particles were obtained in the presence of en and sulfate ions [Fig. 5(a)]. This could be related to the complexing effect of this anion, which is more pronounced than for the other anions studied in this work. In one experiment at an ionic strength of 1.06 mol kg^{-1}, in the presence of en, the ZnO particles were deaggregated [Fig. 5(b)].

The ZnS obtained from the alkaline medium was of poorly defined morphology and at the highest pH value used (pH 13.0) a gelatinous precipitate was obtained. However, when thermal treatment at 60 °C was performed on solutions at pH 6.0, nearly spherical submicrometre particles were obtained for both en and tea ligands (Fig. 6). The effect of the ligand on the shape of the ZnS particles was not as marked as the results for the ZnO powders. The SEM results for ZnS suggest that the best defined and most uniform morphologies are obtained in the presence of tea. Agglomeration is marked in both cases. The fact that the experiments were performed at pH 6.0 means that both en and tea will be partially protonated; however, the ionization of the ligand is promoted by coordination and marked effects upon particulate formation are observed. When the temperature of the solutions is increased the agglomeration of the ZnS particles is promoted and their size is greater for similar

Table 5 Published[27] stability constants (25 °C and $I = 0.1$ mol kg^{-1}) for complexes of zinc and the ligands used in this work

| ligand	equilibrium	log K
mea	ML/M.L	2.70[a]
	ML$_2$/M.L^2	4.78[a]
tea	ML/M.L	2.05
	ML$_2$/M.L^2	3.28
ammonia	ML/M.L	2.21[b]
	ML$_2$/M.L^2	4.50[b]
	ML$_3$/M.L^3	6.86[b]
	ML$_4$/M.L^4	8.89[b]
diethylamine	ML/M.L	2.97
	ML$_2$/ML.L	2.60
	ML$_3$/ML$_2$.L	2.34
	ML$_4$/ML$_3$.L	1.92
	ML$_4$/M.L^4	9.83
en	ML/M.L	5.7
	ML$_2$/M.L^2	10.6
	ML$_3$/M.L^3	12.6
dien	ML/M.L	8.8
	ML$_2$/M.L^2	14.5
trien	ML/M.L	12.0
EDTA	ML/M.L	16.5
NTA	ML/M.L	10.7
	ML$_2$/M.L^2	14.2
OH$^-$	ML/M.L	5.0[b]
	ML$_2$/M.L^2	11.1[b]
	ML$_3$/M.L^3	13.6[b]
	ML$_4$/M.L^4	14.8[b]
	M$_2$L/M^2.L	5.0[b]

[a] $I = 0.5$ mol kg^{-1}. [b] $I = 0$ mol kg^{-1}.
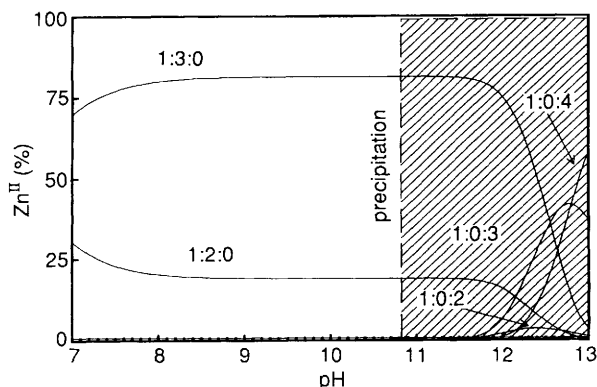
Fig. 9 Speciation diagrams of the zinc–ethylenediamine system at room temperature (25 °C), using the values of Table 5, for the system [Zn^{2+}]:[en] = 1 : 5, [Zn^{2+}] = 0.02 mol l^{-1}. Species as M$_a$(en)$_b$(OH)$_c$.

aging times. Fig. 7 shows such effects for particles obtained at 100 °C.

Use of FTIR Absorption Spectra in Powder Characterization

The morphological characteristics of small particles can, for ionic oxides of well defined shape, have a marked effect on the IR spectrum due to dipole oscillations induced by the vibrational modes. Applying a generalized theory of the dielectrics, Hayashi et al. successfully interpreted the experimental IR spectra[24] of zinc oxide. A theoretical IR spectrum for particles with a defined shape and state of agglomeration can be derived by adjusting a shape factor, g, and a filling factor, f. The influence of the shape and agglomeration state of the ZnO particles on the transverse optical modes, $W_{T\perp} = 377$ cm^{-1} and $W_{T\parallel} = 406$ cm^{-1}, can be studied.

The ZnO particles described in this work present sufficiently specific morphologies for an attempt to correlate shape and spectra.[24-26] Even though the preparation of the KBr pellets

must lead to some changes in the particles, sufficient morphological differences remain for distinct spectra to be observed for different samples (Fig. 3). The FTIR spectra of some of the ZnO powders are shown in Fig. 8. The spectra are characteristic of zinc oxide and no organic or carbonate residues were detected in the spectra. However, some differences in the band profiles can be seen for the different ZnO samples.

Sample D consists of small nodular particles in which aggregation is facilitated, and a single band at 443 cm^{-1} is observed. The samples A, B and C have preferential growth along the c axis, and show splitting of the absorption band. These results agree well with those reported by others.[24,26]

Conclusions

The results of this study suggest that the organic ligand not only inhibits Zn(OH)$_2$ precipitation, allowing a controlled synthesis of ZnO, but can also play a specific role in controlling the growth of the particles under different orientations. The morphological characteristics of the ZnO particles depend both on the presence of organic ligands and their chemical nature.

LaMer and Dinegar[15] claimed that the morphology of colloidal particles is controlled by the speciation of the solution present during the nucleation and growth of the particulate materials, and this idea appears to be confirmed by our observations. The lack of thermodynamic and kinetic data for these systems under the conditions used does not allow a thorough discussion of this hypothesis. However, the stability constants available[27] (Table 5), although determined for other conditions, show that the solution speciation should be quite different for the range of ligands used. A simple calculation (carried out with the program SPECIES, Dr. L.D. Pettit, University of Leeds) suggests that the zinc:en system (1 : 5) at room temperature is unstable with respect to the precipitation of the hydroxide at pH 10.85 whereas the zinc–tea (1 : 5) system becomes unstable at ca. pH 7.0 (Fig. 9). Undoubtedly both thermodynamic and kinetic factors are important in the control of the precipitation mechanism of ZnO and ZnS particulates. SEM results show clearly that the organic ligands strongly influence the powder properties of both materials when they are obtained from solutions where they are present.

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