# Studies on a new method of preparation of zinc sulphide useful for luminescent phosphors

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Hitherto the zinc sulphide material required for luminescent phosphors has usually been obtained by the reaction between a zinc salt and hydrogen sulphide. In this paper we report a new method of preparation of zinc sulphide by the reaction between thiourea and a zinc salt in an alkaline medium, at optimum conditions of pH. The zinc sulphide precipitate obtained under varying conditions of pH has been characterized by the methods of X-ray diffraction, electron microscopy and diffraction, optical microscopy, magnetic susceptibility, diffuse reflectance and density. A very important point which came out of these investigations is that with varying pH for the precipitating conditions, varying degrees of non-stoichiometry have been obtained. All these aspects have been discussed in terms of interstitial zinc atoms or $Zn^+$ ions and electrons in anion vacancies.

## Introduction

Extensive literature [1–5] exists on the synthesis of zinc sulphide phosphors. All the methods are based on the precipitation of zinc sulphide by hydrogen sulphide under varying conditions of pH, anions, etc.

Kramareva *et al.* [6] studied the preparation of zinc sulphide with thiourea in ammonia solution obtaining the final product in two steps: (1) by precipitation of a product containing 14–20% basic salt and (2) by digestion of the product for several hours with alkaline thiourea. Similarly, a French patent [7] refers to the preparation of zinc sulphide using an ion exchange method for purification and subsequent heating to 90°C of a buffered solution containing the purified zinc salt and thiourea and a USSR patent [8] refers to the preparation of zinc sulphide from a soluble zinc salt and thiourea from an ammoniacal medium in the presence of borax as an additive. These methods are time-consuming and involve two or more steps and are not less laborious than the method of preparation of zinc sulphide using hydrogen sulphide gas. The following investigations report a single step precipitation of zinc sulphide using thiourea and a soluble zinc salt under controlled conditions of pH. The conditions of precipitation and the characteristics of zinc sulphides obtained by this method are reported herein.

## Experimental

The principle on which this new method [9] is based consists in taking a mixture of a soluble organic or inorganic zinc salt and an organic sulphur compound like thiol, thiourea, substituted alkyl thioureas, thioacetamide or some inorganic thiocompounds like thiosulphate in aqueous solution at the laboratory temperature and adding an aqueous solution of an alkali hydroxide such that the pH is between 10 and 13 when the desired precipitate of zinc sulphide is thrown out. Instead of a soluble zinc salt the starting material can be zinc oxide dissolved in strong alkali. The precipitation is near completion in about an hour and can be completed in half of this time by sufficient stirring. The zinc sulphide obtained by this method can be easily activated by suitable doping and heat treatment to bring about the solid state reactions. Some of the freshly precipitated undoped samples ob-

*Table 1. Physical characteristics of the precipitated zinc sulphide samples*

| Sample no. | Concentration of NaOH (% w/v) | pH of the solution | Yield (wt in g) | Yield (%w/w) | $\chi$ (in $10^{-6}$ C.G.S. units) | Density (g/cm$^3$) | $\lambda_c$ |
|---|---|---|---|---|---|---|---|
| 1 | 20 | 12·375 | 0·46265 | 47·51 | −0·1840 | 2·816 | 355 nm |
| 2 | 15 | 12·625 | 0·38355 | 38·39 | −0·1479 | 3·441 | |
| 3 | 10 | 12·800 | 0·35875 | 36·84 | −0·2200 | 3·247 | |
| 4 | 5 | 13·000 | 0·59636 | 61·24 | −0·3660 | 2·912 | 340 nm |
| 5 | 1 | 12·600 | 0·92720 | 95·21 | −0·1620 | 4·171 | — |

Concentration of $ZnSO_4.7H_2O$    0·1 M
Concentration of thiourea         0·2 M
$\lambda_c$ = The long wave length absorption edge
$\chi$ = magnetic susceptibility

tained by the above method are weakly photo-luminescent due to self-activation.

Mixtures were made from aqueous standard solutions of zinc sulphate ($ZnSO_4.7H_2O$ 'Analar' grade), thiourea (pure USSR) and sodium hydroxide ('Analar' grade) such that the ternary mixture was of constant volume of 100 ml in all the cases, the concentrations of zinc sulphate and thiourea being kept constant at 0·1 M and 0·2 M respectively in all the mixtures, the variable factor being the concentration of the added sodium hydroxide. As soon as the sodium hydroxide was added the pH of the mixture was measured using a Leeds and Northrup pH meter type 7401 with a suitable glass electrode. To ensure that there are no adsorbed hydroxyl ions in the final product, the precipitated zinc sulphide was thoroughly washed with distilled water, then with a 1% solution by volume of glacial acetic acid and then finally

with distilled water by decantation. All experiments were conducted in polythene beakers around 32°C. Results obtained are given in Table 1.

Another set of experiments were made keeping zinc sulphate and sodium hydroxide concentrations the same in the ternary mixture but varying only the concentration of thiourea. The pH of the mixture and yield obtained in this set of experiments are represented in Table 2.

**Measurements**

*Magnetic susceptibility, density and diffuse reflectance spectra*

All measurements were carried out around a temperature of 32°C. Magnetic susceptibility measurements made for the zinc sulphide precipitates are represented in Table 1. Gouy's

*Table 2. Variation of yield with concentration of thiourea*

| No. | Concentration of thiourea (molarity) | pH | Yield (wt. in g) | Yield (% w/w) |
|---|---|---|---|---|
| 1 | 0·10 | 12·8 | 0·37820 | 38·8 |
| 2 | 0·20 | 13·0 | 0·59635 | 61·24 |
| 3 | 0·30 | 12·9 | 0·68505 | 70·35 |
| 4 | 0·40 | 12·9 | 0·80580 | 82·75 |
| 5 | 0·50 | 12·95 | 0·97231 | 99·85 |
| 6 | 0·60 | 12·9 | 0·97200 | 99·20 |

Concentration of $ZnSO_4.7H_2O$     0·1 M
Concentration of sodium hydroxide    5% w/v

method was used for the measurements. A Polytronic Electromagnet type EM-100 giving a field of about 5000 gauss at 3 A for a pole-gap of 3 cm was used. For calibration and measurements on zinc sulphide powders a standard technique described by Bates [10] was used. The susceptibility tube was a 20 cm long flat-bottomed glass tube of uniform bore (0·4 mm) with a ground glass stopper and an arrangement on top for suspension.

Weighings were made with an H 16 'Mettler' semimicro-balance (single pan) of capacity 80 g and precision 0·01 mg provided with a hanger for suspending the susceptibility tube below. The balance was kept on a platform 75 cm high from the centre of the pole-gap in order to avoid any disturbance by the magnetic field during weighings.

The susceptibility tube was suspended by means of a nylon thread so that the bottom of the tube was at the centre of the gap between the two poles. To enhance accuracy, the suspension system and the susceptibility tube were kept in a draught-proof box provided with a door in front, through which, with a long shaft and knob arrangement, the balance beam could be manipulated.

The zinc sulphide samples were finely powdered in an agate mortar and packed in the susceptibility tube by adding small and approximately equal layers and gently tapping the bottom of the tube on the bench after addition of each layer. French and Harrison [11] investigated the application of a correction for the air enclosed in the packed solid. They showed that the experimentally determined susceptibility of a powdered sample is the same by all methods provided the packing is uniform throughout the packed column.

The equation used by us is similar to that derived by French and Harrison (loc. cit.). The mass susceptibility $\chi$ of the powdered sample is given by

$$\chi = \frac{2\Delta wgl}{H^2W} + \frac{K_2}{d} \qquad (1)$$

where $\Delta w$ is the difference in weight due to the applied magnetic field '$H$' at the centre of the gap, $W$, the weight of the sample filling the tube, $d$, the density of the sample and $K_2$, the volume

susceptibility of air. As the length of the column is the same throughout $H^2/2gl$ is taken as the instrument constant $C$. Hence from Equation (1), $C$ is given by

$$C = \Delta w \cdot \frac{d}{W} \cdot \frac{1}{K_1 - K_2} \qquad (2)$$

where $K_1$ and $K_2$ are the volume susceptibilities of the solid and air respectively. The value of $C$ was determined by using the solid calibrant, cane sugar, whose susceptibility is already known. Hence by substituting the values for $K_1$, the volume susceptibility of the calibrant and $K_2$, that of air from International Critical tables, $C$ was calculated.

Substituting $C$ for $H^2/2gl$ in equation (1) we have

$$\chi = \frac{\Delta w}{WC} + \frac{K_2}{d}$$

The correction due to the susceptibility tube was applied to the $\Delta w$ values.

The densities of the samples were determined by the displacement method using benzene.

Diffuse reflectance spectra of the zinc sulphide powders were obtained with a Beckmann Model DU Spectrophotometer in conjunction with an 1P 28 Photomultiplier using chemically pure MgO as the standard sample. Results obtained for the different zinc sulphide samples presented in Table 1 are represented in Fig. 1. The $\lambda$ (cut off) was obtained by plotting the Remission Function $R$ ($f$) versus $\lambda$, wherein

$$R(f) = \frac{(1-R)^2}{2R},$$

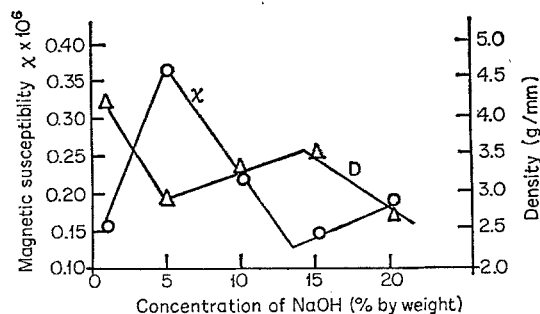$R$, being the diffuse reflectance [24].



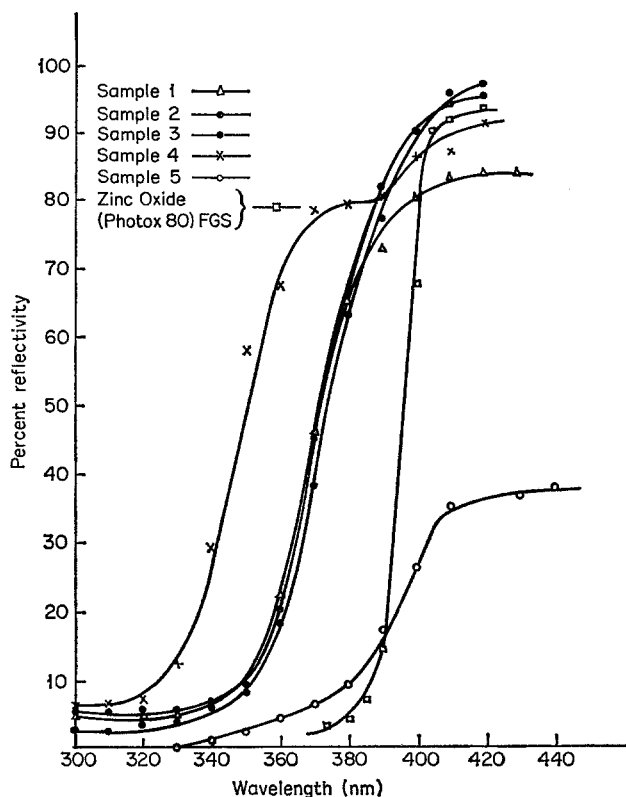Fig. 1. Diffuse reflectance spectra of zinc sulphide powders.

Fig. 2. Data of the physical characteristics of various zinc sulphide
samples presented in Table 1.

*X-ray diffraction data*

X-ray diffraction powder data on samples of
zinc sulphide represented in Table 1 are given in
Table 3. The X-ray diffraction powder pattern
was taken in a Philips X-ray diffractometer with
$CuK_\alpha$ (Ni-filtered) radiation at 36 kV, 16 mA.
The 8d8 values were calculated using $\lambda_{CuK\alpha} =$
1·5418 Å taking the weighted average of
$\lambda_{CuK\alpha1} = 1·54050$ Å and $\lambda_{CuK\alpha2} = 1·54434$ Å in
the intensity ratio of 2:1.*

The data could be indexed most satisfactorily
on the basis of a cubic unit cell of zinc sulphide
with $a = 5·40$ Å. The structure is described by
Wyckoff [12] to be face-centred cubic. Each
atom has about it four equally distant atoms of
the opposite sort arranged at the corners of a
regular tetrahedron.

There is a fairly good agreement between the
X-ray data obtained in the present study and
those reported by Gerlach et al. [13] The three

* The authors wish to express their thanks to the
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the X-ray diffraction powder pattern of the samples.

strongest lines namely (111), (220) and (311) for
each of the patterns of Gerlach et al. and the
A.S.T.M. pattern are also the strongest lines
obtained in this present study. It is clear that the
chemically prepared samples 1 to 4 conform to
the beta-zinc sulphide structure. Here $I/I_1$
denotes the relative intensities of the lines on the
X-ray diffraction pattern referred to the strong-
est line as 100%. The pattern of sample 5 cor-
responds to that of zinc oxide reported by
Weber et al. [14] and by the A.S.T.M.

*Electron microscopic studies*

Electron microscopic and diffraction studies were
made with a Philips EM-75 Electron Microscope
capable of giving a maximum magnification of
12 000 and a resolution of 50 Å. Electron
diffraction patterns confirm the X-ray diffrac-
tion data that all the first four zinc sulphide
samples are of the sphalerite structure (beta). An
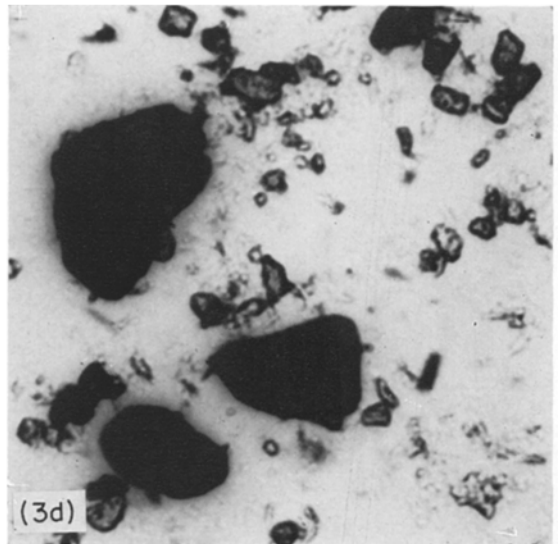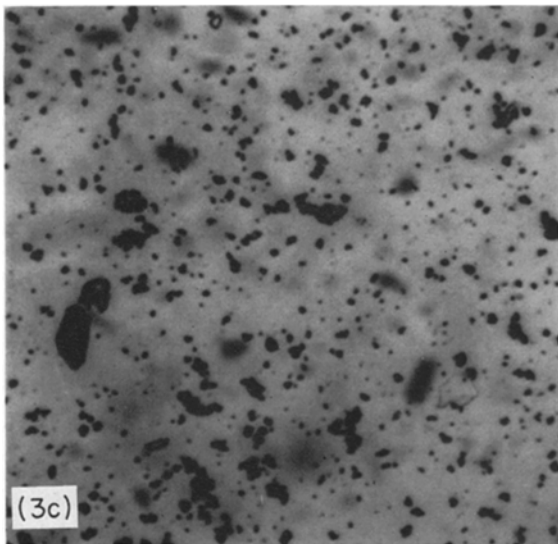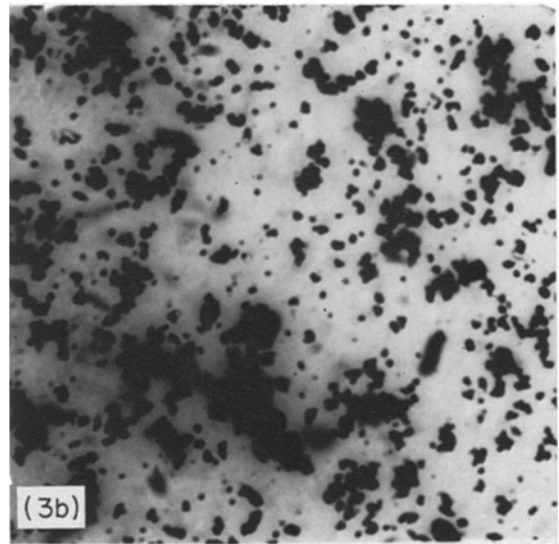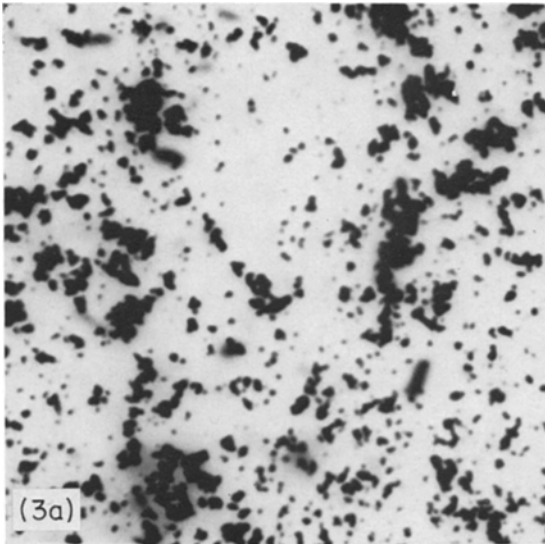electronmicrograph for sample (5) is shown in
Fig. 6.

Fig. 3. Graphite powder. ($\times$ 60 000).

*Table 3. X-ray diffraction powder data obtained on samples reported in Table 1*

| hkl | $d_{theor}$ | Sample 1 | | Sample 2 | | Sample 3 | | Sample 4 | |
|---|---|---|---|---|---|---|---|---|---|
| | | $d_{obs}$ | $I/I_1$ | $d_{obs}$ | $I/I_1$ | $d_{obs}$ | $I/I_1$ | $d_{obs}$ | $I/I_1$ |
| 111 | 3·097 | 3·086 | 100 | 3·097 | 100 | 3·093 | 100 | 3·072 | 100 |
| 220 | 1·894 | 1·896 | 38 | 1·879 | 40 | 1·879 | 40 | 1·861 | 45 |
| 311 | 1·63 | 1·639 | 30 | 1·63 | 32 | 1·6142 | 31 | 1·6059 | 36 |
| 222 | 1·575 | 1·60 | 34 | — | — | 1·54 | 31 | — | — |

Sample No. 5

| hkl | 100 | 002 | 101 | 102 | 110 | 103 | 200 | 112 | 201 |
|---|---|---|---|---|---|---|---|---|---|
| $d_{theor}$ | 2·81 | 2·61 | 2·46 | 1·90 | 1·63 | 1·48 | 1·42 | 1·38 | 1·36 |
| $d_{obs}$ | 2·82 | 2·61 | 2·47 | 1·91 | 1·625 | 1·48 | 1·408 | 1·38 | 1·359 |
| $I/I_1$ | 66 | 67 | 100 | 23 | 32 | 29 | 8 | 24 | 14 |

*Optical microscopic studies*

A Reicherts' Universal Camera Microscope was used. The freshly precipitated sample powders were used as such by dispersing in an organic solvent, i.e. without disrupting the crystallites by grinding or any such process. Figs 3 and 4 are the micrographs under a magnification of 240. The patterns of the corresponding unground samples may be compared with the electron micrographs in Fig. 5.

**Results and discussion**

Table 1 as well as Fig. 2 indicate that the yield of ZnS precipitated depends on the concentration of sodium hydroxide employed. Incidentally it is
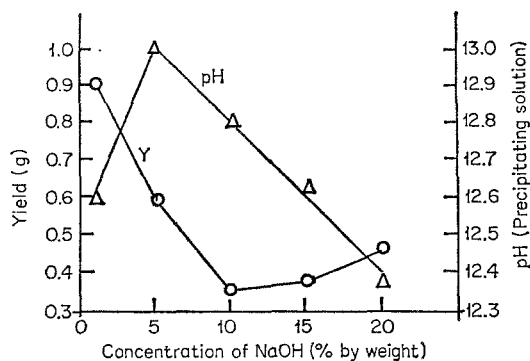


Fig. 3. Photomicrographs (× 240) of zinc sulphide obtained at various concentrations of sodium hydroxide: (a) 20% w/v; (b) 15% w/v; (c) 10% w/v; and (d) 5% w/v.

very interesting to note that the curve of pH of the precipitating bath versus the concentration of sodium hydroxide shows a peak at 5% w/v sodium hydroxide.

All the five samples precipitated were examined to see whether they were pure zinc sulphide or admixtures of zinc sulphide with zinc oxide. With this object in view, making use of the fact that zinc oxide is fairly soluble in moderately dilute acetic acid whereas zinc sulphide is insoluble, weighed quantities of the five samples were each treated with 50% v/v solution of acetic acid, washed thoroughly with distilled water by decantation, filtered in sintered crucibles, dried at 120°C in an air oven, cooled and weighed. The first four samples were practically constant in weight whereas the fifth sample showed a considerable reduction of approximately 0·65 g. The first four samples precipitated were zinc sulphide samples whereas the fifth sample was an admixture of zinc oxide with zinc sulphide. The above experimental results were further confirmed by the X-ray and electron diffraction patterns obtained for the corresponding samples. Also the X-ray diffraction data presented in Table 3 confirm that all the first four samples are of zinc sulphide belonging to the sphalerite (β) structure and the fifth sample is zinc oxide. Similarly the diffuse reflectance spectral curve of sample 5 in Fig. 1 shows deviation from the curves of ZnS and ZnO. The first four zinc sulphide samples were

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white in colour whereas the last one containing zinc oxide was yellow in colour. It is reported in the literature [4, 15] that zinc sulphide containing predominantly zinc oxide is coloured yellow.

The curves representing the variation of magnetic susceptibility ($\chi$) and density respectively with concentration of sodium hydroxide given in Fig. 2, make an interesting study. The density value of $\beta$-ZnS calculated from the NBS lattice constants is 4·096 g/cm³ at 26°C [16]. That the density of our zinc sulphide samples varies between 2·816 and 3·441 g/cm³ indicates the existence of considerable non-stoichiometry in our samples. Confining ourselves to a discussion of only the first four samples of zinc sulphide precipitated, we may examine the diffuse reflectance spectra in conjunction with the density and magnetic susceptibility variations. It is most significant from the figure giving diffuse reflectance spectra that of the four samples, only sample 4 (precipitated at a concentration of 5% NaOH) has an absorption edge of 340 nm [15, 17] (corresponding to a band gap of 3·636 eV). This coincides with the reported value of 341 nm (which corresponds to a band gap of 3·647 eV) for $\beta$-ZnS [4, 18, 19]. The other samples, viz. sample nos. 1 to 3 precipitated at sodium hydroxide concentrations of 20%, 15% and 10% (w/v) respectively, have an almost identical absorption edge at 355 nm corresponding to a band gap of 3·493 eV, shifted to the longer wave length side.

The above facts require explanation. Zinc sulphide is known to be of n-type. In the band model of zinc sulphide, $Zn^+$ ions are known to be at the foot of the conduction band and the $S^{2-}$ ions at the top of the valence band [20, 21, 22]. The accepted band gap is 3·64 eV [4, 18, 19] for $\beta$-ZnS. It is necessary to explain why the three zinc sulphide samples precipitated at concentrations of 10%, 15% and 20% (w/v) of sodium hydroxide have an identical band gap smaller than the accepted value of 3·64 eV. The progressive fall in the diamagnetic susceptibility of the precipitated zinc sulphide samples with increasing concentration of sodium hydroxide implies that the level of $Zn^+$ ions is built up interstitially below the conduction band. A clue to this implication is obtained from the diffuse

reflectance curve of sample 4 which shows a shoulder developing around 390 nm, just starting on a region common to the diffuse reflectance curves of samples 2 and 3. In this connection the work of Seitz [23], in which he reported the atomic absorption spectrum of interstitial Zn atoms, may be recalled. The zinc sulphides precipitated with increasing concentration of sodium hydroxide show a progressive fall in the diamagnetic susceptibility values from sample 4 to 2. Subsequently as one proceeds to sample 1 the diamagnetic susceptibility increases and the density falls. As zinc atoms are more diamagnetic than $Zn^+$ ions one may have to assume that as the precipitation conditions change from sample 2 to 1 more $Zn^+$ ions give place to Zn atoms. In the process of the formation of $Zn^+$ ions in the earlier samples, a progressive fall of diamagnetism from sample 4 to 2 implies a process of charge compensation by which perhaps single electrons are left behind in the anion vacancies. When we go to sample 1 a slight increase in diamagnetism implies the using up of single electrons in anion vacancies by the $Zn^+$ ions to form zinc atoms. This explains the slight increase in the diamagnetism and a fall in the density, which necessarily results when a negative electron is removed from an anion vacancy. The increase in density from sample 4 to 2 supports the progressive building up of the interstitial $Zn^+$ ions. All the reported values of susceptibility are diamagnetic. The zinc atom being more diamagnetic than the $Zn^+$ ion it may be more accurate to presume that the interstitials are made up of both $Zn^+$ ions and zinc atoms. The fall of diagmagnetic susceptibility values from sample 4 to 2 may be due to an increase in the ratio of $Zn^+$ ions to zinc atoms ($Zn^+$/Zn) which undergoes an inversion in going from sample 2 to 1, also exhibited in the density variation from sample 2 to 1. The diffuse reflectance spectrum curve of sample 1 shows that the limiting value of the diffuse reflectance from 380 nm, is about 80% showing perhaps a saturation of the interstitial levels. This is in contradistinction to the diffuse reflectance curves of samples 3 and 2 which reach a diffuse reflectance value of about 100% beyond 400 nm.

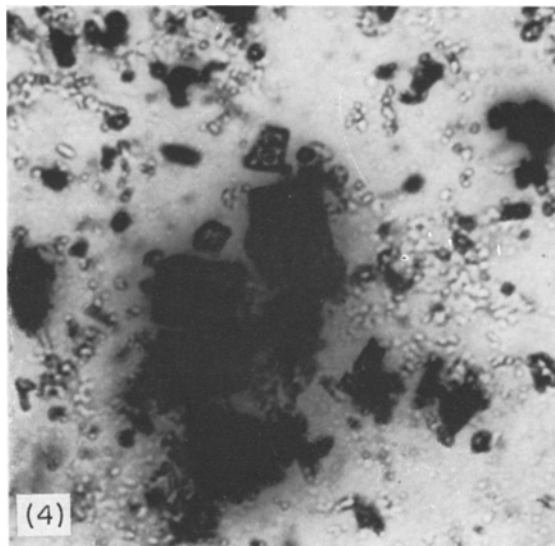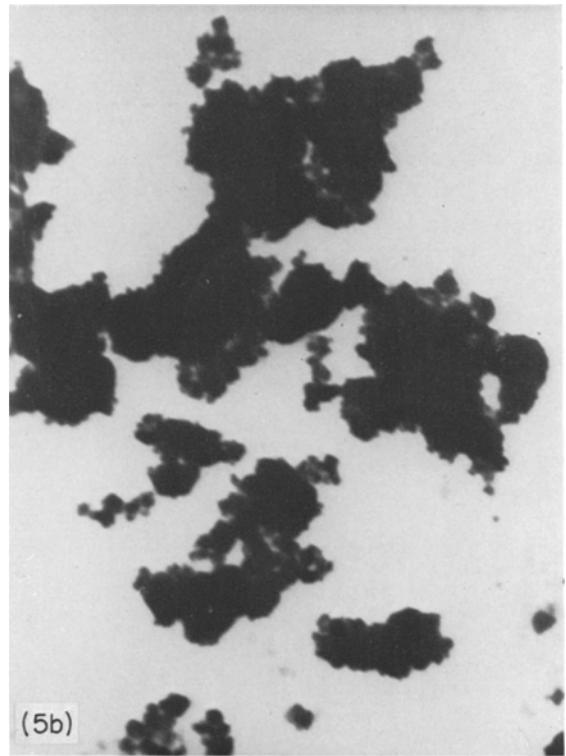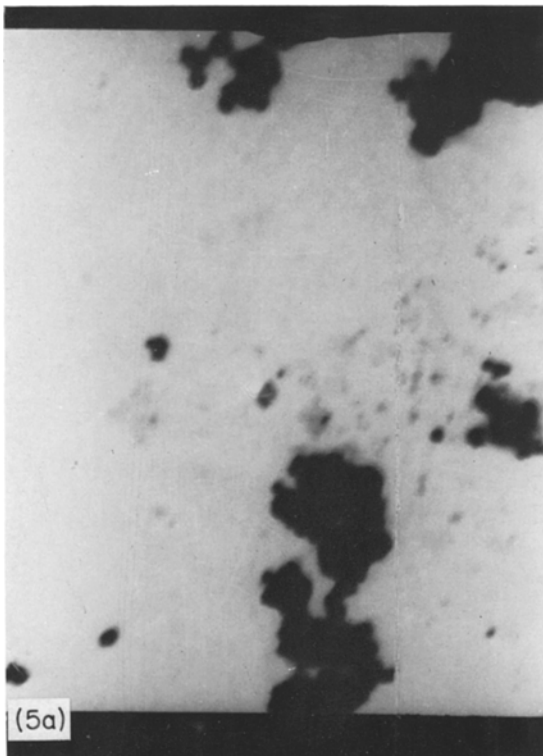The above investigation shows that the conditions of precipitation of zinc sulphide from

Fig. 4. Photomicrograph (×240) of zinc sulphide containing a large amount of zinc oxide obtained at sodium hydroxide concentration of 1% w/v.
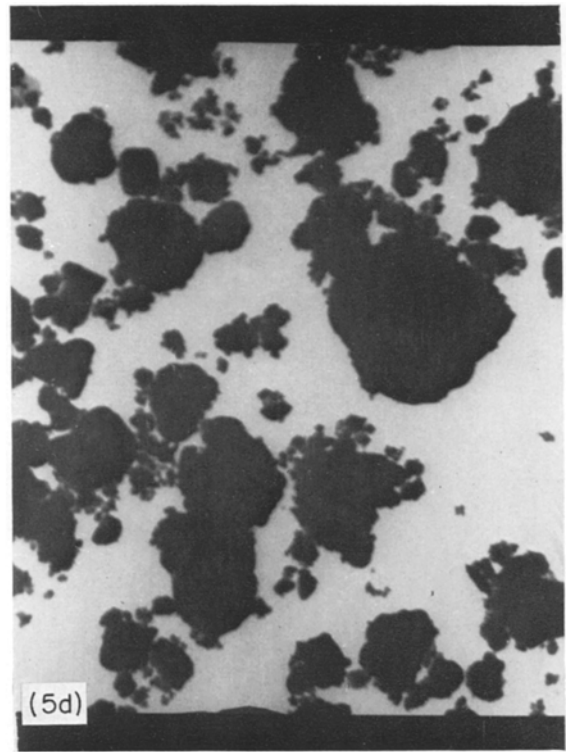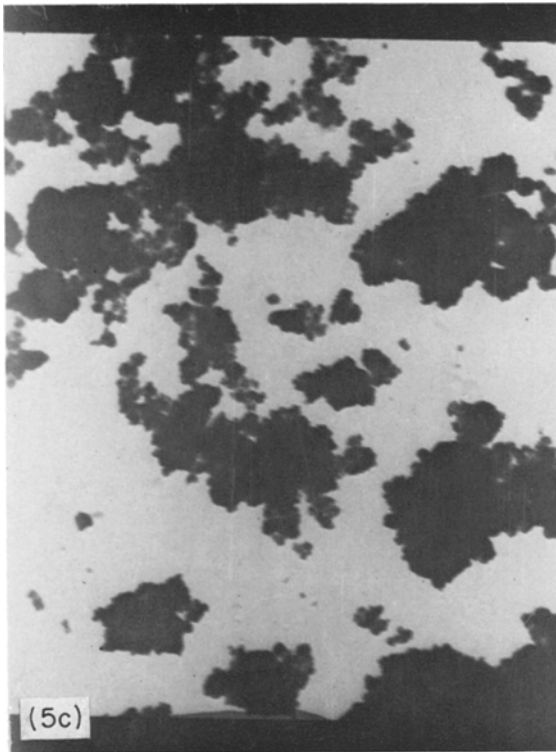
Fig. 5. Electronmicrographs (×1200) of zinc sulphide obtained at various concentrations of sodium hydroxide: (a) 20% w/v; (b) 15% w/v; (c) 10% w/v; and (d) 5%w/v.
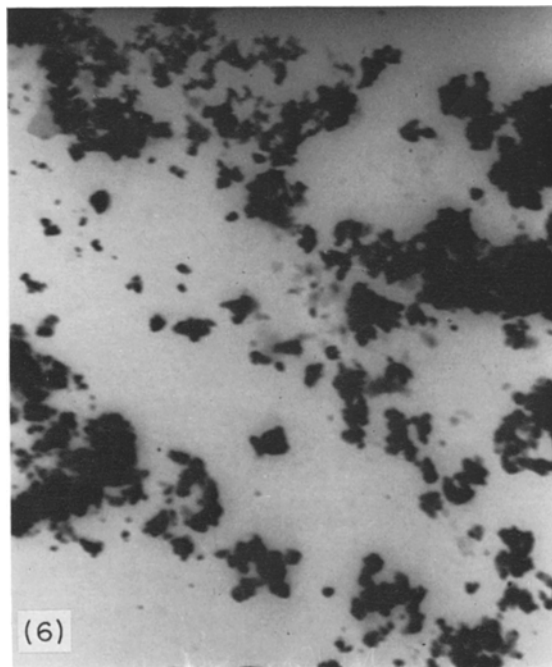


Fig. 6. Electronmicrograph (×1200) of zinc sulphide containing a large amount of zinc oxide obtained at sodium hydroxide concentration of 1% w/v.

alkaline thiourea solutions influence the non-stoichiometry to a considerable extent such that the absorption edge is also modified due to levels of interstitial $Zn^+$ ions and zinc atoms being built up below the conduction band.

Fig. 3 a, b and c as well as electron-micrographs a, b and c of Fig. 5 respectively show up the particles of zinc sulphide samples 1, 2 and 3. They are all uniformly fine in size and similar in nature. Fig. 3 d and Fig. 5 d show that the sample of zinc sulphide number 4 consists of some larger aggregates of particles. Fig. 4 and Fig. 6 show crystals which are predominantly zinc oxide.

It is interesting to note that the four samples of zinc sulphide studied were precipitated under conditions of gradually varying pH. The pH variation of the precipitating baths is linear in the range in which the zinc sulphide samples were precipitated. The non-stoichiometry of the powders and the $Zn^+$ levels introduced in the zinc sulphide samples seem to have some systematic relation with the pH of the bath.

## Acknowledgement

## References

[1] A. L. Smith, *J. Electrochem. Soc.*, **93** (1948) 324.
[2] W. Van Gool, *Philips Res. Rept. Suppl.*, 3 (1961) 6.
[3] A. A. Bundel and G. V. Zhukov, *Opt. Spectrosc. USSR*, **18** (1965) 270.
[4] F. A. Kröger and J. M. Dikhoff, *J. Electrochem. Soc.*, **93** (1948) 156.
[5] G. R. Levy and C. G. Fontana, *Attiv. Accad. Zag. Lincei*, 7 (1928) 502.
[6] T. V. Kramareva, L. A. Kosareva and V. M. Schulman, Khalkogenidy (Svoista, Methody Poluch. Primen), Mater Seminara, Ist Kiev (1965) 86.
[7] French Patent Number 1388522 (1965).
[8] USSR Patent Number 276929 (1970).
[9] Indian Patent Number 126439 (1971).
[10] L. F. Bates, 'Modern Magnetism', Cambridge University Press, London (1963).
[11] C. F. French and D. Harrison, *J. Chem. Soc.*, Part III, (1953) 2538.
[12] R. N. G. Wyckoff, 'Crystal Structure', Chapter III, p. 19 (John Wiley, Interscience, New York) (1922).
[13] W. Gerlach, *Phys. Z.*, **23** (1922) 114.
[14] L. Weber, *Z. Krist.*, **57** (1922) 398.
[15] F. A. Kröger and J. M. Dikhoff, *J. Electrochem. Soc.*, **99** (1952) 144.
[16] National Bureau of Standards Circular 539, Vol. II.
[17] J. H. Gisolf, *Trans. Faraday Soc.*, **35** (1939) 90.
[18] Peter Pringsheim, 'Fluorescence and Phosphorescence', John Wiley Interscience, New York (1949).
[19] Charles Kittel, 'Introduction to Solid State Physics', Asia Publishing House, London (1962).
[20] Aldert van der Ziel, 'Solid State Physical Electronics', Macmillan, London (1958).
[21] Frederic Seitz, 'The Modern Theory of Solids', McGraw-Hill, New York (1940).
[22] V. S. Kulkarni and D. S. Ambardekar, *J. Shivaji Univ.*, **2** (1969) 63.
[23] F. Seitz, *Trans. Faraday Soc.*, **35** (1939) 98.
[24] P. Kubulka, and F. Munk, *Z. tech. Physik.*, **12** (1931) 593.