Production of Microcrystalline Zinc Sulphide at Low Temperatures

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The conditions for obtaining zinc sulphide through slow crystallization from a solution with a low concentration of zinc and sulphide ions are investigated in this paper. Electron microscopic studies reveal a tenfold growth of the sulphide crystals as compared to those obtained by the usual precipitation process of passing hydrogen sulphide through a zinc salt solution. X-ray analysis shows their sphalerite structure. The luminophore which was prepared by "cold" activation was of a low intensity and had an emission maximum in the long wave range.

1. Introduction

Zinc sulphide powders employed as luminophores are usually prepared through precipitation by passing hydrogen sulphide through a zinc salt solution. The degree of the sulphide's crystallinity depends not only on the pH, but also on the temperature and the nature of the solution in which the precipitation takes place. Of great importance is a low level of oversaturation, which ensures a low velocity of seed formation, which can be attained through a low sulphide ion concentration and correspondingly a low pH of the solution. On this basis Ortmann and Piwonka [1] have developed a method for the production of well crystallised zinc sulphide by slow precipitation with hydrogen sulphide, strongly diluted with nitrogen. The aim of the present paper is to propose a method for the preparation of microcrystalline zinc sulphide by maintaining a constant low concentration of the zinc ions, while keeping a low pH of the solution. To this end zincoxalate was used, which on the one hand has a low solubility, and on the other hand, being a salt of a strong acid, helps to ensure a low pH, and consequently a low concentration of sulphide ions.

2. Experimental

The zinc oxalate and carbonate were prepared from a zinc sulphate solution and the corresponding precipitants. The oxalate was obtained by interaction at a high temperature (80 °C) of a zinc sulphate solution with oxalic acid, the latter taken in excess as regards to the stoichiometrically needed quantity. The precipitant for the zinc carbonate was $NaHCO_3$ saturated in advance with carbon dioxide and cooled in a cooling mixture (ice and salt). The zinc sulphate solution, also cooled beforehand, was combined with the bicarbonate solution and the resultant mixture was left for several hours in the cooling system. In this way a voluminous precipitate of zinc carbonate was obtained.

The transformation of the oxalate and the carbonate into sulphides was done in the following way: suspensions of these salts were saturated with hydrogen sulphide at 80 °C, and after having been continuously stirred for 2–3 hours, were left for several days in a closed system. Under these conditions, about 20% of the ZnC_2O_4 and 25% of the $ZnCO_3$ were transformed into sulphide. The rest of the carbonate and the oxalate which did not take part in the interaction were removed by dissolving in concentrated ammonia.

3. Results and Discussion

The samples obtained in different ways underwent X-ray analysis, the results of which are shown in Fig. 1. According to the data given in literature, peaks at $\theta = 14^\circ 28'$, $23^\circ 72'$, $28^\circ 72'$, $38^\circ 82'$, $44^\circ 18'$, and $47^\circ 64'$ correspond to the α-modification of ZnS.

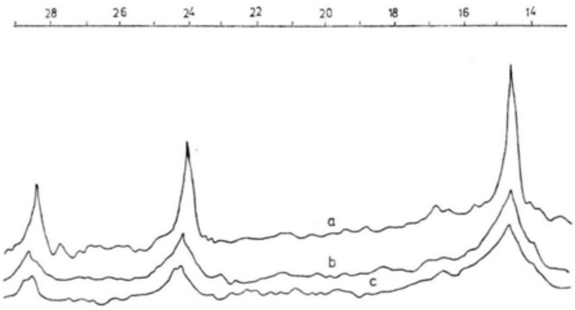

Fig. 1. a) ZnS prepared from ZnC_2O_4, b) ZnS prepared from $ZnCO_3$, c) ZnS prepared from $ZnSO_4$.

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When these are compared to the maxima observed, it becomes evident that all the samples have a sphalerite structure.

As to the degree of crystallinity, the best results are obtained when zinc oxalate is used. The band width ΔH is 0.35° for the sulphide prepared from oxalate, as compared to $\Delta H = 1.15°$ for the sulphide precipitated from zinc sulphate. This is due to the small solubility product of the oxalate and consequently low concentration of zinc ions ($\approx 3 \cdot 10^{-5}$ g-ion/l) and also to the low pH (at pH-1, the sulphide ion concentration is $\approx 10^{-19}$ g-ion/l). These factors determine the low velocity of the sulphide's precipitation in a zinc oxalate solution, exacting to large crystals.

Electron microscopic photographs showed the particles to be 0.5 μ in diameter for the sulphide prepared from the oxalate and 0.01 μ in diameter for the sulphide prepared from the sulphate solution.

Experiments were made for the activation with Mn of a sulphide prepared from an oxalate. The luminophores had the luminescence characteristics of manganese, although of low intensity. The emission spectra of the samples with activator concentrations 10^{-2} g-atom Mn/mol ZnS are shown on Figure 2. The emission is weakest for the sample prepared by coprecipitation of zinc and manganese ions as oxalates with following transformation into sulphides (curve 1). The intensity is greater if of activator ions are introduced into the zinc oxalate suspension as $MnCl_2$ (curve 2). The sample with the highest intensity of luminescence was prepared through contact activation of the sulphide with an $MnCl_2$ solution (curve 3). In all cases the emission spectrum was greatly expanded and the maximum was displaced toward longer waves ($\lambda_{max} = 650$ nm) compared to ZnS-Mn activated at above 800 °C [2], and also to a "cold" activated luminophore [3] with $\lambda_{max} = 605$ nm. Contact activation can be connected with the adsorption of manganese aquocomplexes at the surface of the crystals and thus a different environment of the activator as compared to ZnS-Mn activated at high temperature. This can explain the appearance of longer wave components in the emission spectrum, whose overlapping results in the wide spectrum displaced toward longer waves.

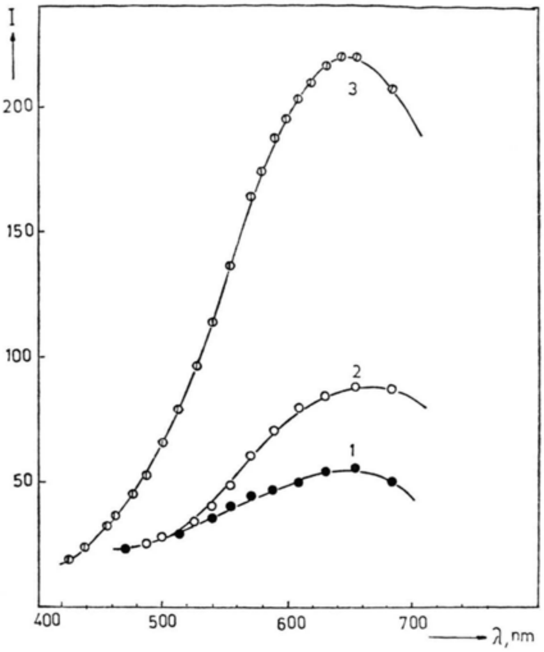

Fig. 2. ZnS-Mn emission spectra.

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[2] R. H. Bube, Phys. Rev. **90**, 70 (1953).

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