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Technical Report No. 3

CHEMICAL PRECURSORS TO ZINC SULFIDE: ZnS WHISKER SYNTHESIS

by

T. A. Guiton, C. L. Czekaj, M. S. Rau, G. L. Geoffroy, C. G. Pantano

Prepared for Publication in  
Better Ceramics Through Chemistry III,  
MRS 1988

July 11, 1988

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The Pennsylvania State University  
Departments of Chemistry and Materials Science and Engineering  
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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION / AVAILABILITY OF REPORT APPROVED FOR PUBLIC RELEASE DISTRIBUTION UNLIMITED	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) #3		5. MONITORING ORGANIZATION REPORT NUMBER(S) N0014-86-K0191	
6a. NAME OF PERFORMING ORGANIZATION The Pennsylvania State University	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research Dr. R. Schwartz	
6c. ADDRESS (City, State, and ZIP Code)		7b. ADDRESS (City, State, and ZIP Code) Code 3854 Naval Weapons Center China Lake, CA 93555	
8a. NAME OF FUNDING / SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code)		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Chemical Precursors to Zinc Sulfide: ZnS Whisker Synthesis			
12. PERSONAL AUTHOR(S) T. A. Guiton, C. L. Czekaj, M. S. Rau, G. L. Geoffroy, C. G. Pantano			
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) July 11, 1988	15. PAGE COUNT 6
16. SUPPLEMENTARY NOTATION in Print, Better Ceramics Through Chemistry III, MRS 1988			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) A variety of reactions employing organometallic precursors have been explored for the synthesis of ZnS. One of the most successful routes involves the reaction of [EtZn(SBu <sup>t</sup> ) <sub>5</sub> ] with H <sub>2</sub> S at ambient or sub-ambient temperature to yield a precipitate which is subsequently heated under flowing H <sub>2</sub> S at 500°C to yield a mixture of sub-micron particles and single-crystal ZnS whiskers. Transmission electron micrographs of the [EtZn(SBu <sup>t</sup> ) <sub>5</sub> ] products indicate that the ZnS morphology is critically dependent upon the rate of H <sub>2</sub> S reaction. Corresponding x-ray/electron diffraction, electron microscopy, elemental analysis, NMR and infrared spectroscopies have been conducted. A summary of the chemical methods, product characterization results, and proposed synthesis mechanisms will be presented.			
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION	
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

# CHEMICAL PRECURSORS TO ZINC SULFIDE: ZnS WHISKER SYNTHESIS<sup>†</sup>

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## ABSTRACT

A variety of reactions employing organometallic precursors have been explored for the synthesis of ZnS. One of the most successful routes involves the reaction of  $[\text{EtZn}(\text{SBU}^t)]_5$  with  $\text{H}_2\text{S}$  at ambient or sub-ambient temperature to yield a precipitate which is subsequently heated under flowing  $\text{H}_2\text{S}$  at  $500^\circ\text{C}$ . to yield a mixture of sub-micron particles and single-crystal ZnS whiskers. Transmission electron micrographs of the  $[\text{EtZn}(\text{SBU}^t)]_5$  products indicate that the ZnS morphology is critically dependent upon the rate of  $\text{H}_2\text{S}$  reaction. Corresponding x-ray/ electron diffraction, electron microscopy, elemental analysis, NMR and infrared spectroscopies have been conducted. A summary of the chemical methods, product characterization results, and proposed synthesis mechanisms will be presented.

## INTRODUCTION

As the mechanical, thermal, electrical, and chemical requirements for advanced optical components become more rigorous, the processing control of powder morphology becomes exceedingly critical. For example, one approach to improving the mechanical properties of a material is to form a self-similar composite. This is essentially the concept demonstrated by E. Fitzer and co-workers for  $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$  fiber reinforced composites in which a three-fold increase in fracture toughness from  $4\text{MNm}^{1/2}$  for polycrystalline  $\text{Al}_2\text{O}_3$  to  $12\text{MNm}^{1/2}$  for fine-grained  $\text{Al}_2\text{O}_3$  containing 40%  $\text{Al}_2\text{O}_3$  fibers was illustrated [1].

Currently, CVD derived ZnS is one of the most widely used infrared optical window materials. Unfortunately, for numerous applications it does not possess optimum mechanical properties. To fabricate infrared transmitting ZnS/ ZnS composites requires the development of high aspect ratio, micron sized ZnS whiskers. No present methodology exists for the convenient, large-scale preparation of such whiskers. Although larger ZnS single crystals and whiskers have been made by a variety of high temperature routes ( $> 900^\circ\text{C}$ ) [2-5], alternative routes have been sought for greater ZnS whisker morphology control. Low temperature organometallic routes are attractive for this purpose, and we report herein a novel route to micron sized ZnS whiskers using a combination of organo-zinc compounds with sulfur delivery agents.

## EXPERIMENTAL

The precursor compound used in this study is the known pentameric species  $[\text{EtZn}(\text{SBU}^t)]_5$ , prepared by the reaction of  $\text{Et}_2\text{Zn}$  with  $\text{Bu}^t\text{SH}$  (60-85% yield) [6]. This compound is oxygen sensitive, and thus, is synthesized by standard air sensitive techniques. When  $\text{CH}_2\text{Cl}_2$  solutions of these species at  $22^\circ\text{C}$  were exposed to  $\text{H}_2\text{S}$  gas at flow rates varying from 5-85 cc/min, a white precipitate immediately deposited. The solution above the precipitate was removed by cannula, and the precipitate was dried in air. This ZnS precursor was then thermally treated in a tube furnace under a flowing  $\text{H}_2\text{S}$  atmosphere to a maximum temperature of  $500^\circ\text{C}$  using  $\text{H}_2\text{S}$  flow rates of 20, 35, and 75 cc/min. The resulting products were analyzed as described below.

<sup>†</sup>The authors gratefully acknowledge the Office of Naval Research for the support of this research under Contract N0014-86-K-0191.



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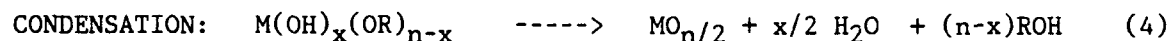
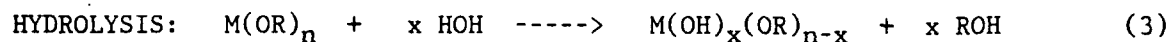
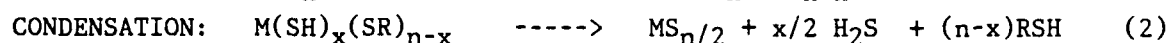
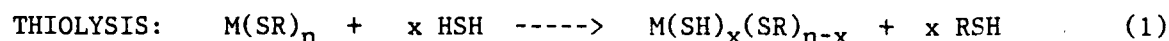
## RESULTS AND DISCUSSION

Significant morphological transformations occurred as a function of flow rate of H<sub>2</sub>S during both the solution reaction and the thermal treatment. Each will be treated separately and observations will be correlated to analogous oxide sol/gel chemistry.

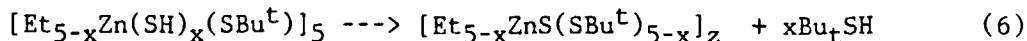
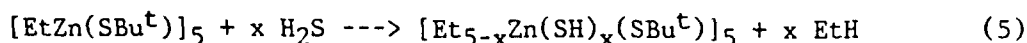
### Solution Reaction Products

The [EtZnSBu<sup>t</sup>]<sub>5</sub> pentamer precursor (Figure 1A) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and then reacted with H<sub>2</sub>S. As Figure 1 illustrates, the morphology of the solution product is critically dependent upon the rate of H<sub>2</sub>S flow and thus the extent of H<sub>2</sub>S reaction. At 5 cc/min, a fibrous chainlike product results (Figure 1B); at 40 cc/min, fibrous and particulate products result (Figure 1C); while at 85 cc/min, a fine particulate powder results (Figure 1D). <sup>1</sup>H-NMR of the solutions indicate the formation of Bu<sup>t</sup>SH and EtH upon addition of H<sub>2</sub>S. This result correlates with the solution product infrared spectra (Figure 2). The infrared spectra, in addition to powder x-ray diffraction (Figure 3), further verify the chemical and structural transitions, i.e., the transformation from the amorphous pentamer precursor to the crystalline ZnS powder product, and thus the extent of reaction as a function of H<sub>2</sub>S flow rate.

Presumably, upon contact with H<sub>2</sub>S, the pentamer undergoes a thiolysis/condensation reaction, analogous to metal alkoxide hydrolysis/condensation reactions:



Given the pentameric structure of [EtZn(SBu<sup>t</sup>)]<sub>5</sub> and the observations that 1) EtH and Bu<sup>t</sup>SH are immediately formed upon contact with H<sub>2</sub>S and 2) no -SH modes were evident in the infrared spectra, it is concluded that the thiolysis step is rapid and first involves Zn-Et bond cleavage, then Zn-S-Bu<sup>t</sup> bond cleavage, followed by the formation of Zn-S-Zn linkages to form an extended ring-chain network:



Hence, it is proposed that the morphology is a direct result of the extent of thiolysis and condensation. Initially, as the polymeric pentamer's organic ligands are terminated, the pentamer's structure is fibrous chains. As the thiolysis reaction proceeds, the extent of Zn-S-Zn crosslinking increases, and the resulting product is a fine nano-scale ZnS powder. This is evident when examining the infrared spectra. At 5 cc/min the pentamer has undergone minimal thiolysis; whereas, at 85 cc/min, the pentamer has undergone extensive thiolysis. Furthermore, x-ray diffraction, selected area diffraction (SAD) and FTIR Far IR analysis verify that the 85 cc/min product is composed of agglomerates of 3.8-6.6 nm ZnS particles.

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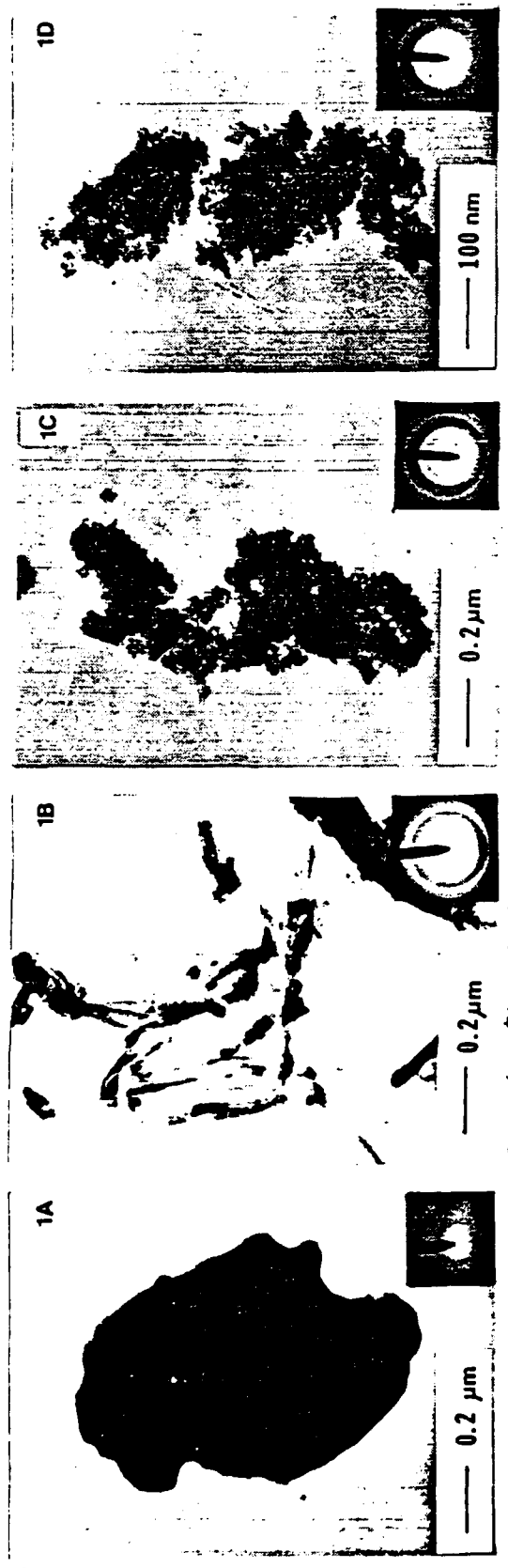


Figure 1.  $[\text{EtZn}(\text{SBu}^t)]_5$  (1A) hydrolysis products as a function of  $\text{H}_2\text{S}$  flow rate: 5 cc/min (1B), 40 cc/min (1C), 85 cc/min (1D).

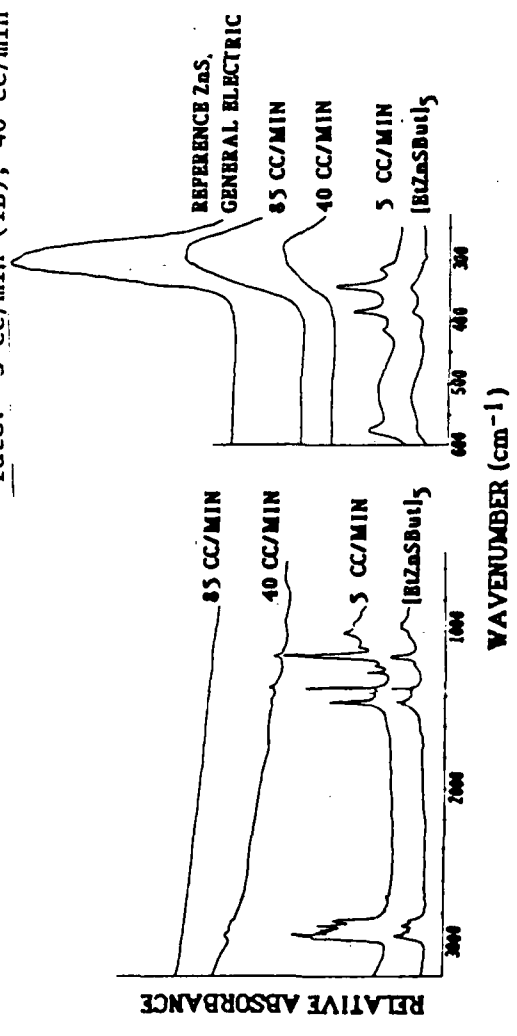


Figure 2. FTIR spectroscopy of  $[\text{EtZn}(\text{SBu}^t)]_5$  solution products.

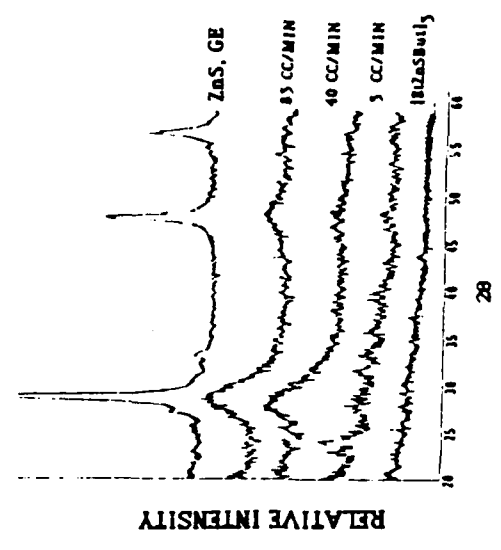


Figure 3. Powder x-ray diffraction of  $[\text{EtZn}(\text{SBu}^t)]_5$  solution products.

## Thermal Treatment Products

In an effort to remove residual organic ligands, the two morphologically extreme solution derived products, the 5 cc/min fibrous precursor and the 85 cc/min particulate precursor, were thermally treated ( $T_{\text{max}}=500^{\circ}\text{C}$ ) under a flowing  $\text{H}_2\text{S}$  atmosphere as a function of time and flow rate.

The 85 cc/min precursor comprised of agglomerates of 3.8-6.6 nm powders (Figure 4a) was heat treated at  $500^{\circ}\text{C}$  for 1 and 2 hours (Figures 4B-4C) under a 20 cc/min  $\text{H}_2\text{S}$  flow. As determined by TEM convergent beam diffraction and powder x-ray diffraction (Figure 5), the resulting products were  $\beta\text{-ZnS}$  single crystal powders averaging 39nm after 1 hour and 48nm after 2 hours. FTIR analysis confirmed the removal of residual organic ligands and the existence of ZnS (Figure 6) as referenced to optical grade ZnS (General Electric) powders.

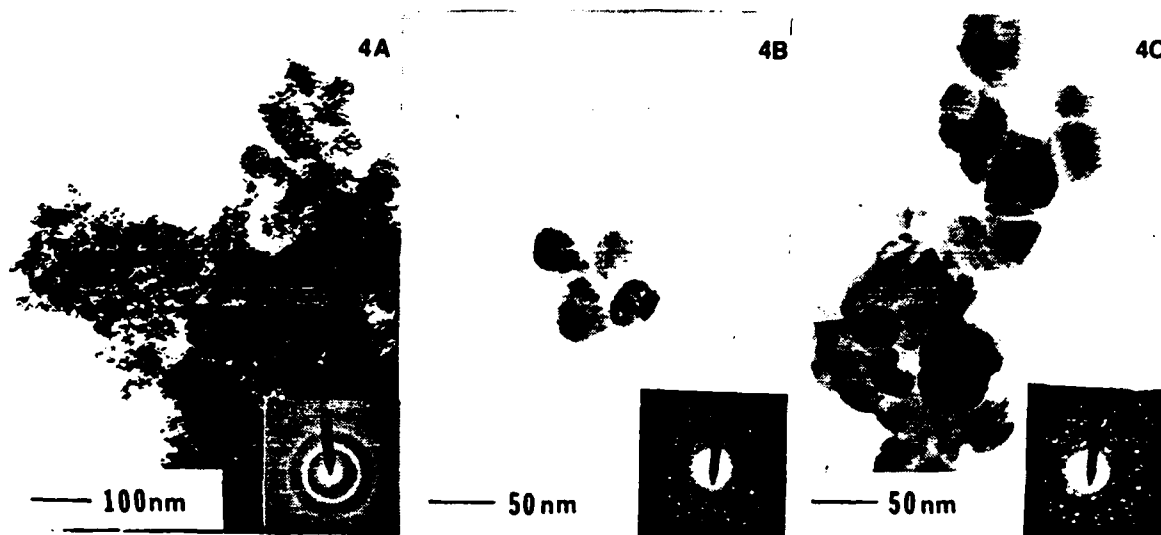


Figure 4.  $[\text{EtZn}(\text{SBu}^t)]_5 + \text{H}_2\text{S}$  (85 cc/min) precursor (4A) thermally treated ( $500^{\circ}\text{C}$ ) products, 20 cc/min  $\text{H}_2\text{S}$ , 1 hour (4B) and 2 hours (4C) at.

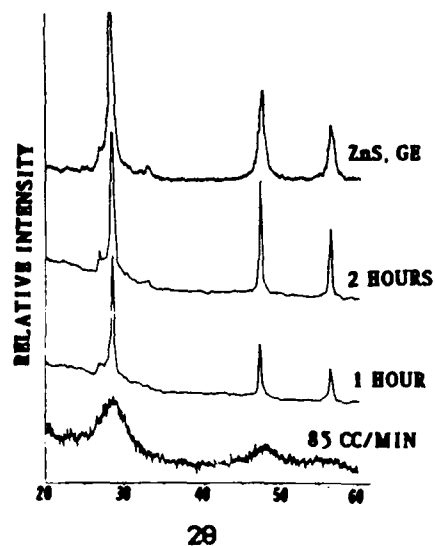


Figure 5. Powder x-ray diffraction of 85 cc/min thermally treated products.

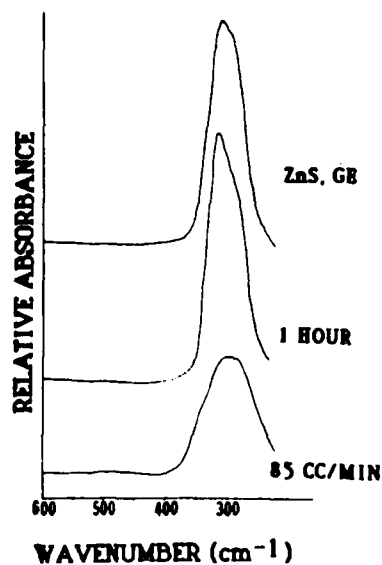


Figure 6. FTIR spectroscopy of 85 cc/min thermally treated products.

Figure 7 illustrates the significant morphological transformations which occurred when the fibrous 5 cc/min precursor (Figure 7A) was thermally treated at 500°C for 1, 2, and 8 hours at 20 cc/min (Figures 7B-7D) and at 75 cc/min (Figures 7E-7G) H<sub>2</sub>S flow rates. In contrast to the 85 cc/min precursor products (Figure 4), both of the 5cc/min systems result in single crystal ZnS whiskers. The most striking transformations occur at the 75 cc/min H<sub>2</sub>S flow rate. After 1 hour, the fibrous features of the precursor result in terminated chains of ZnS powders, 6.2-12.4nm (Figure 7E). While, after 2 hours at 500°C, the resulting products are single crystal  $\alpha$ -ZnS whiskers (Figure 7F, 500nm length, aspect ratio 11). TEM SAD and x-ray powder diffraction confirm the  $\alpha$ -ZnS whisker, wurtzite, 2H structure (JCPDS File 36-1450). Typical whiskers range from 400 to 1000 nm in length with aspect ratios ranging 10-18. Upon extended thermal treatment, up to 8 hours, the resulting products are sub-micron (average 110nm), single crystal powders (Figure 7G). The 20 cc/min H<sub>2</sub>S thermal treatment products also result in single crystal whiskers after 1 (Figure 7B) and 2 hour heat treatments. Similarly, the 8 hour thermally treated products are sub-micron single crystal powders (Figure 7D, 250-450 nm). FTIR analysis of the thermally treated products confirm the loss of occluded organics and the development of the characteristic ZnS fundamental mode at 320 cm<sup>-1</sup>.

We suggest that the powders and whiskers form by two different processes. As previously discussed (Equations 5-6), the first step in the reaction of the pentameric precursor with H<sub>2</sub>S involves cleavage of the Zn-Et bonds and Zn-SBu<sup>t</sup>, followed by Zn-S-Zn polymerization. After extended thiolysis, the solution reaction yields a highly cross-linked, three dimensional network. Other work on polymeric ceramic precursors has shown that highly-cross linked polymers tend to yield ceramic powders upon pyrolysis [7]. Thus, the powder formation can be assumed to derive from pyrolysis of the initially formed polymeric network.

The ZnS whiskers are believed to form by a process related to the established high temperature chemical transport routes (>900°C) to ZnS whiskers. Our low temperature route presumably involves a similar process in which the organo-metallic polymeric precursor reacts with H<sub>2</sub>S to form a volatile product which subsequently condenses yielding a whisker morphology. Consistent with this suggestion is the observation that the high organic, fibrous 5 cc/min precursor (Figure 1B) yields  $\alpha$ -ZnS whiskers at 20-75 cc/min H<sub>2</sub>S flow rates, while the low organic, highly cross-linked 85 cc/min precursor (Figure 1D) yields  $\beta$ -ZnS powders, but does not yield ZnS whiskers at 20-75 cc/min flow rates.

In summary, we have demonstrated that single crystal ZnS whiskers can be formed by a novel low-temperature organometallic route. The whisker morphology is critically dependent upon the extent of [EtZn(SBu<sup>t</sup>)<sub>5</sub>] thiolysis, and thus network condensation. This work has thus demonstrated the ability to control non-oxide particle morphology via the organometallic approach to synthesis. These whiskers are within the size range required to form optical composites, and experiments are now in progress to fabricate whisker reinforced ZnS/ZnS composite materials.

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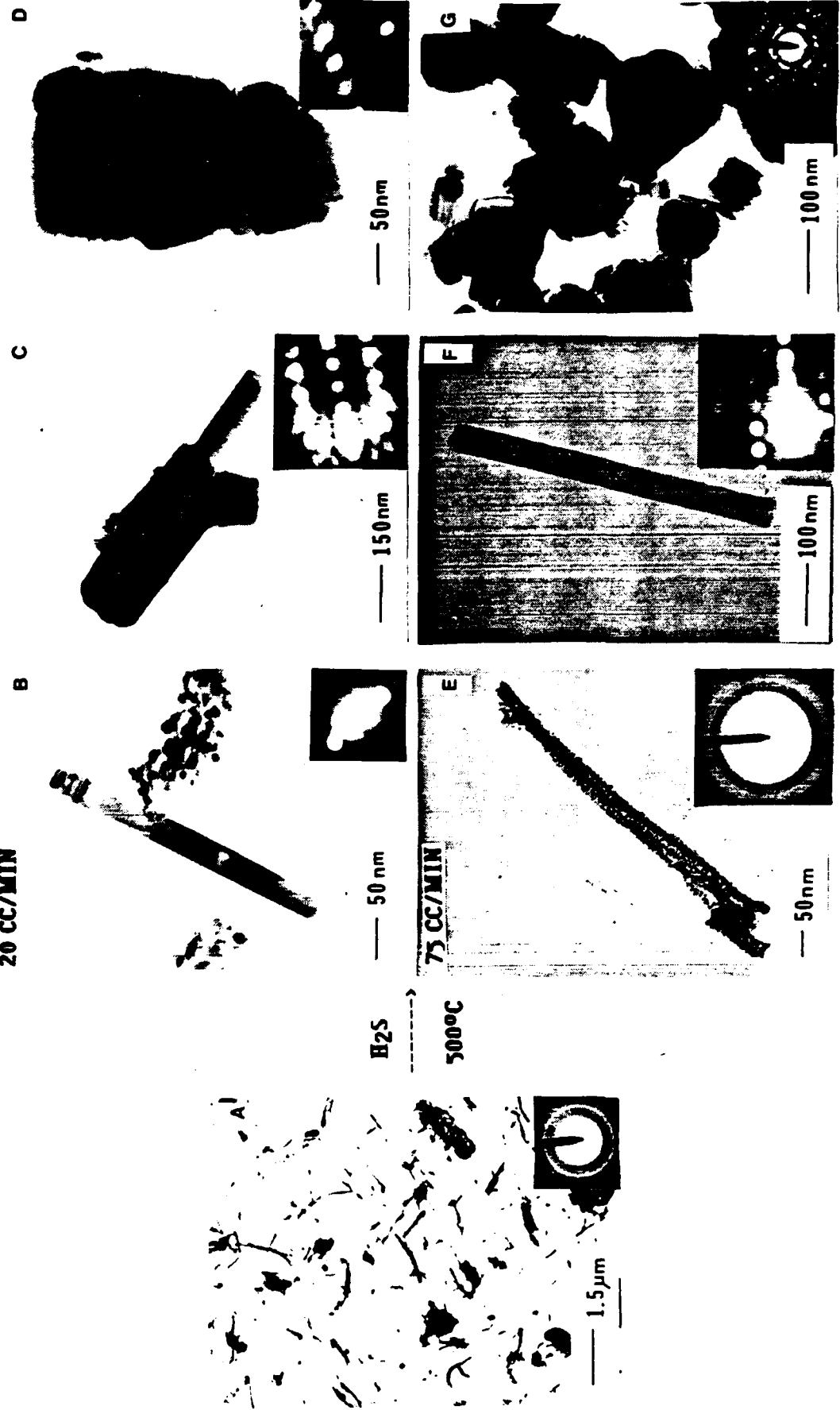


Figure 7.  $[\text{EtZn}(\text{SBu}^t)]_5 + \text{H}_2\text{S}$  (5 cc/min) precursor (7A) thermally treated (500°C) products, at 20 cc/min  $\text{H}_2\text{S}$ , 1 hour (7B), 2 hours (7C), 8 hours (7D) and at 75 cc/min  $\text{H}_2\text{S}$ , 1 hour (7E), 2 hours (7F), 8 hours (7G).