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AN ORGANOMETALLIC ROUTE TO MICRON-SIZED WHISKERS OF
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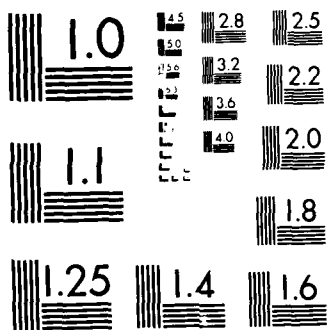
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AN ORGANOMETALLIC ROUTE TO MICRON-SIZED WHISKERS OF ZINC
SULFIDE

BY

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AN ORGANOMETALLIC ROUTE TO MICRON-SIZED WHISKERS OF ZINC SULFIDE

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ABSTRACT: Sub-micron particles and single crystal whiskers of ZnS have been prepared in a two step process involving the reaction of $\{\text{EtZn}(\text{SBU})\}_5$ with H_2S at sub-ambient temperature followed by a 500°C heat treatment under flowing H_2S .

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AN ORGANOMETALLIC ROUTE TO MICRON-SIZED WHISKERS OF ZINC SULFIDE

Sir:

↙ A number of technologies require the development of high performance optical materials that also meet stringent specifications of optical transparency and thermal, chemical, and mechanical properties. ^(1,2) For example, an infrared transmitting window material should have low thermal expansion, high melting and decomposition temperatures, chemical inertness to hydrolysis and oxidation, and high fracture toughness. One of the most attractive materials for many ^{INFRARED} ~~IR~~ optical applications is ^{Zinc Sulfide} ~~ZnS~~, but this material, as presently fabricated, does not possess the required mechanical properties.

One approach to improving the mechanical properties of a material is to form a self-similar composite, ^{4,5} in this case, ZnS whiskers in a polycrystalline ZnS matrix. To fabricate IR transmitting ZnS/ZnS composites, it would be necessary to use micron-sized whiskers of ZnS that have length to width ratios (aspect ratios) greater than 10. No present methodology exists for the convenient, large-scale preparation of such whiskers, although larger single crystals and whiskers of ZnS have been made by a variety of high temperature ($>900^{\circ}\text{C}$), generally vapor-phase, routes. ⁽⁷⁻¹⁶⁾ We have sought alternative methods for producing ZnS whiskers that would give greater control over the product morphology. 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.

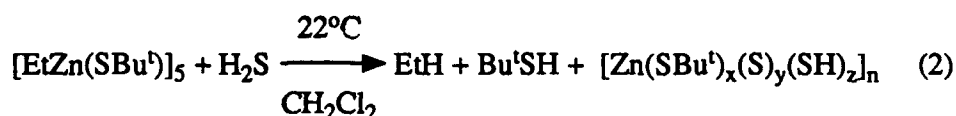
↙ (7-16) ←

The precursor compound used in this study is the pentameric species $[\text{EtZn}(\text{SBu}^t)]_5$ which

is highly soluble in organic solvents.¹⁷⁻¹⁹ This known compound can be synthesized in high yields (60-85%) by the low temperature reaction of Et_2Zn with Bu^tSH , eq. 1.¹⁷ When H_2S gas



was passed over stirred toluene or CH_2Cl_2 solutions of this species at a flow rate of 5 cc/min, a white precipitate immediately deposited, and ^1H NMR analysis indicated the formation of Bu^tSH and EtH . IR and Raman analysis showed the presence of significant quantities of residual organics in this precipitate, and an X-ray powder diffraction analysis gave only a very broad band in the region of the most intense ZnS peak ($3.12\text{\AA}$). Transmission electron microscopy showed this material to have a fibrous morphology, Figure 1, and a weak selected area electron diffraction (SAD) pattern in the TEM analysis indicated the presence of some crystalline ZnS . Elemental analysis showed the presence of Zn/S/C/H in a 1:1:3.9:8.5 atomic ratio,^{20a} again indicating the presence of significant quantities of residual organics. This product is presumably a mixture of amorphous ZnS and an oligomeric species such as that written in eq. 2.



Thermogravimetric analysis of this solid under an N_2 atm gave 11.7% wt loss up to 360°C corresponding to partial loss of the residual organics. After the TGA analysis, the X-ray powder diffraction pattern of the remaining solid showed three broad peaks at d-spacings of 3.11, 1.91 and $1.63\text{\AA}$ characteristic of ZnS , and the typical ZnS diffraction pattern was seen in a TEM-SAD analysis. Elemental analysis of this heat-treated material showed a Zn/S/C/H atomic ratio of 15.3:15.6:1:4.1,^{20b} indicating significant removal of residual organics upon the heat treatment. Note that the Zn/S ratio is close to the 1:1 ratio of ZnS . After this heat treatment under N_2 , electron microscopy showed the product to be highly agglomerated and composed of 5.9-9.6 nm spherical particles, Figure 2.

A significant morphological transformation occurred when the solid product of eq. 2 was heated *under flowing H_2S* at $500^\circ C$ for 2 h.²¹ An X-ray diffraction pattern of the gray powder obtained after this treatment indicated the presence of ZnS, and TEM micrographs, Figure 3, showed the material to be a mixture of 12.2-26.5 nm spherical particles and single crystal whiskers with the latter predominating. TEM-SAD analysis confirmed the whisker phase to be α -ZnS (wurtzite) and the powder to be predominantly β -ZnS (zinc blende). A representative sample whisker, 0.74 μm long with an aspect ratio of 14, is shown in Figure 4. The whiskers typically range from 0.4-10 μm in length with aspect ratios of 10-18. The reaction temperature and H_2S flow rate are critical parameters in determining whether or not whiskers form. No whiskers were observed in experiments in which the furnace temperature was kept below $400^\circ C$ nor when the H_2S flow rate was greater than 100 mL/min. A flow rate of 70 mL/min was optimum. It must be emphasized that the whiskers form only when the sample is heated in the presence of H_2S , and so the H_2S must play a critical role in the morphological change.

A number of observations indicate that the two factors which are critical to the formation of whiskers are the fibrous morphology of the initial precipitate from eq. 2 and the presence of residual organics in the material. As suggested in eq. 2, the first step in the reaction of the pentameric precursor with H_2S presumably involves cleavage of the Zn-Et bonds to yield ethane and Zn-SH groups, and such species should readily polymerize to yield a cross-linked, three-dimensional network. When the H_2S flow rate in reaction 2 is low (5 cc/min), a weakly cross-linked gel-like material containing a substantial amount of residual organics precipitates in the fibrous morphology shown in Figure 1. TEM analysis has shown that when this material is heat treated under H_2S at $500^\circ C$, the fibrous solid progressively changes into a fibrous agglomerate of nanometer sized ZnS particles which then fuse together to form the whiskers observed in Figures 3 and 4. Other work in our laboratory has shown that higher H_2S flow rates (85 cc/min) give instead a highly cross-linked precipitate having a particulate morphology, not

fibrous, and which contains little residual organics. No whiskers form upon 500°C heat treatment of this latter material.

The process by which the nanometer sized ZnS particles fuse together to form the whiskers appears to be related to the established high temperature chemical transport routes to ZnS whiskers. In these methods, a high purity ZnS source is sublimed at $> 900^{\circ}\text{C}$, and the vapor is passed into a temperature gradient where the whiskers grow. Our low temperature route presumably involves a similar process in which the polymeric precursor reacts with H_2S to form a volatile organometallic product that condenses to fuse the nanosized particles together into a whisker morphology. Consistent with this suggestion is the observation that whiskers are never produced if the H_2S flowrate is high, apparently because the volatile ZnS precursors are swept out of the reaction zone. Furthermore, in some of the TEM analyses on the initially formed white powder produced by eq. 1, it was observed that whenever the electron beam was highly focussed, the sample vaporized and condensed onto other parts of the TEM grid in a *fibrous morphology*.

In summary, we have shown that micron-sized single crystal whiskers of ZnS can be reproducibly formed by a novel low-temperature organometallic based route. These whiskers are precisely the size needed to form composites for IR applications, and experiments are currently in progress to fabricate whisker-reinforced ZnS/ZnS composite materials that should have have improved mechanical properties. Those results will be reported in due course.

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- (20) (a) Zn, 39.26%; S, 17.18%; C, 26.01%; H, 4.75%.
(b) Zn, 65.17%; S, 32.53%; C, 0.78%; H, 0.27%.
- (21) The thermolysis was conducted by placing the sample in a pyrex boat in a tube furnace under a flowing H_2S atm (20-75 cc/min). The temperature was ramped from 22°C to 150°C over a 45 min time period and this temperature was held for 2 h. The temperature was quickly increased to 200°C and held for 2 h, then to 250°C and held for 1 h. Finally, the sample was heated to 500°C over a 1 h period and then held at 500°C for 2 h. The whisker formed in the same region of the boat as the initial powder sample.

Figure Captions

Figure 1. Transmission Electron Micrograph of the solid product formed upon reacting $[\text{EtZn}(\text{SBU})]_5$ with H_2S at a flow rate of 5 cc/min in CH_2Cl_2 solution at 22°C .

Figure 2. Transmission Electron Micrograph of the ZnS product formed after heating the sample shown in Figure 1 to 360°C under an N_2 atm.

Figure 3. Transmission Electron Micrograph of the ZnS product formed upon heating the sample shown in Figure 1 at 500°C for 1h under a flowing H_2S atm.

Figure 4. Transmission Electron Micrograph of a ZnS single-crystal wurtzite whisker ($0.74\text{ }\mu\text{m}$ length, $0.05\text{ }\mu\text{m}$ width) selected from the sample shown in Figure 3.



Figure 1

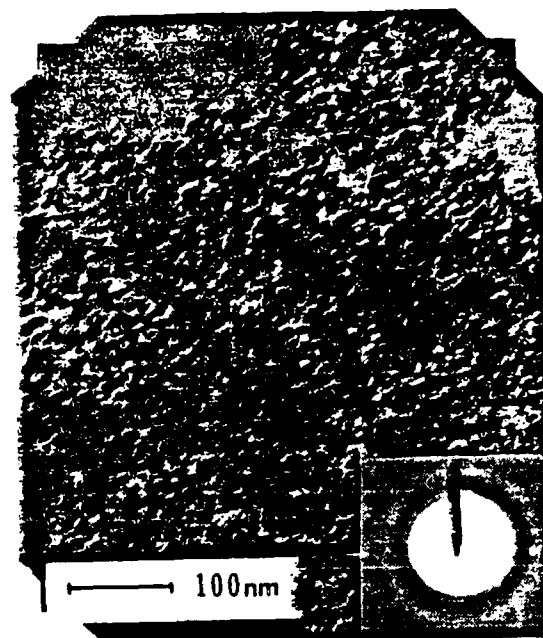


Figure 2



Figure 3

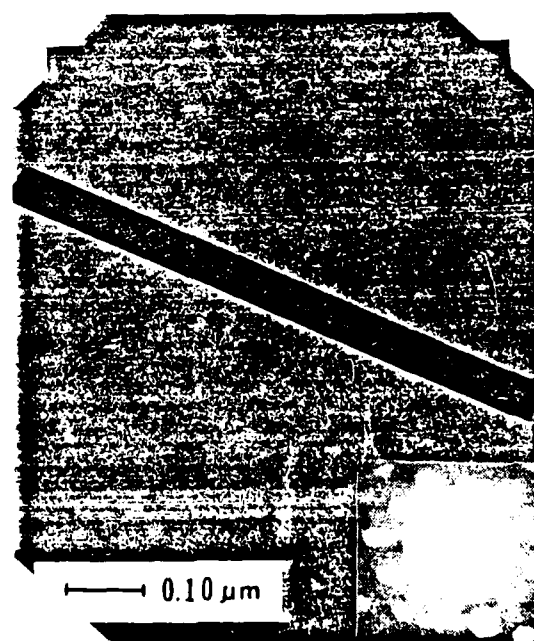


Figure 4

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