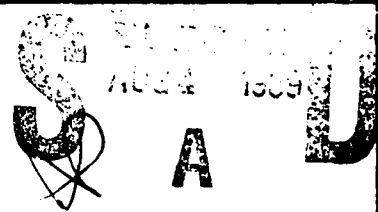


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PREPARATION, PURIFICATION, AND DENSIFICATION OF ZINC SULFIDE POWDER FROM ORGANOMETALLICS

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ABSTRACT

Zinc sulfide powders were prepared from diethylzinc and hydrogen sulfide in toluene solution at -20°C . The powder consisted of agglomerates of $0.1\text{-}\mu\text{m}$ -sized particles. The residual zinc ethyl group content was determined by acid hydrolysis followed by gas chromatography and varied from 10^{-4} to 3 mol % depending on reaction conditions. Reactivity varies with alkyl group as di-*n*-butylzinc > diethylzinc > dimethylzinc. Toluene and isopropylthiol were identified as organic impurities with isopropylthiol originating in the H_2S reagent. Adventitious tetrahydrofuran impurity was converted to tetrahydrothiophene upon heating at 137 to 159°C . Organic impurities were oxidized by treatment of the powder with O_2 at 400°C or 1 mol % O_3 in O_2 at 25°C . Particle growth was evident in the O_2 -treated sample but not in the O_3 -treated sample. The oxidized samples contained about 2 mol % ZnSO_4 and EPR spectra provided evidence for $\text{SO}_2^{\cdot-}$ radicals. The ZnSO_4 impurity was converted to ZnO by heating at 800°C . Hot isostatic pressing of the treated powders at 775°C produced fragmented opaque compacts with grain sizes varying from 0.1 to $0.5\text{ }\mu\text{m}$. The densified samples exhibited about twice the hardness of commercial Raytran™ ZnS but only half the fracture toughness.



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INTRODUCTION

Zinc sulfide is an important infrared optical material.^{1,2} Synthetic routes to ZnS vary from room temperature precipitation in aqueous solutions to high temperature solid state reactions. High temperature methods tend to give highly crystalline products with large grain sizes, while low temperature syntheses can yield powders of uniform submicron particles.³⁻⁶ The latter are desirable for producing high quality fine-grained ceramics.⁷ Aqueous preparations can suffer from oxide impurities due to hydration, and also from anionic impurities.

We are interested in organometallic routes to ZnS powders. Organometallic reagents have potential advantages of high purity, high reactivity, and use in nonaqueous environments. Dimethylzinc and diethylzinc have been used to make ZnS thin films by reaction with H₂S, in the temperature range of 350 to 750°C.⁸⁻¹⁰ Ethyl (t-butylthio) zinc pentamer forms submicron particles and single crystal whiskers of ZnS when subjected to a two step treatment with H₂S at 22 and 500°C.¹¹ Oligomeric bis(methylthio) zinc forms ZnS when heated at 260-280°C.¹² We have examined the utility of the reaction of homoleptic metal alkyl complexes with H₂S in toluene solution for the preparation of metal sulfide powders.¹³ In this paper we describe our efforts to synthesize submicron ZnS powder, purify it of organic impurities, and convert it into a fine-grained ZnS ceramic with potentially improved mechanical properties. Preliminary reports have appeared¹⁴⁻¹⁶ as well as an independent report on the preparation of ZnS powder doped with amine ligands by the reaction of diethylzinc with H₂S in ether solution.¹⁷

EXPERIMENTAL SECTION

General. The following reagents were used as received: H_2S (Matheson, C.P., 99.5% min), benzene- d_6 (MSD Isotopes, 99.6 atom % D min), and 38% DCl in D_2O (ICN, 98%). Diethylzinc (Aldrich) was fractionally distilled under argon at 113 to 115°C and its purity checked by ^1H NMR spectroscopy. Samples typically contained methyl-zinc group impurities consistent with 0.3% Me_2Zn . Toluene (Burdick and Jackson spectrophotometric grade) was distilled from sodium. Oxygen was dried by passing through P_4O_{10} . Argon (Matheson, prepurified, 99.998%) was purified by passage through MnO and molecular sieve columns.¹⁸ Dimethylzinc¹⁹ and di-*t*-butylzinc²⁰ were prepared by literature methods. Waste H_2S was destroyed by passing through concentrated NaOCl solutions. Air-sensitive reagents were transferred and stored in a helium-filled glove box. Glassware was dried in an oven at 200°C before use.

Ozone was generated by passing oxygen through a glass condenser across which a high voltage electric field was provided by a 12,000 V (60 mA) neon sign transformer.²¹ To measure ozone production, the gas from the generator was bubbled through a 50 mL graduated cylinder containing 1.0 g of KI in 40 mL of water. The liquid was transferred to a beaker, treated with 0.3 g of *N*-2-hydroxyethylpiperazine-*N'*-2-ethanesulfonic acid (HEPES buffer) to raise the pH to near 6.3, and titrated with 0.023 M sodium thiosulfate. An ozone concentration of 1.1 mol % was found for a 200 mL/min oxygen flow rate. For treatment of ZnS powder, the ozone from the generator was conducted through glass tubing to the bottom of a 90-mm glass frit on which the powder was placed.

Heating experiments were conducted with a Jetrus Technical Products H.M. pot furnace (95 mm deep x 21 mm inner diameter using a long-necked quartz sample flask with a 14/35 inner joint) or a Lindberg Type 55035 tube furnace (37 cm long with a 30 mm outer diameter quartz tube). Temperature was measured with a thermocouple placed in contact with the sample

container. IR spectra were recorded on a Nicolet 60SX spectrophotometer equipped with a Barnes diffuse reflectance cell. X-ray powder diffraction patterns were obtained from vaseline or acetone-slurry mounted samples on glass slides or "zero-background" off-axis cut quartz using a Scintag PAD V diffractometer with $\text{CuK}\alpha$ radiation. ^1H NMR spectra (80.13 MHz) were recorded on an IBM NR80 Fourier transform spectrometer. Chemical shifts were referenced to the residual solvent peak (benzene- d_5 7.15 ppm) or, for aqueous solutions, to added 3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt (Aldrich). Scanning electron micrographs (SEM) were obtained on an Amray Model 1400 instrument. Auger electron spectroscopy was conducted on a PHI 600 scanning Auger microscope. Gas chromatographic analysis of hydrocarbon gases was performed on a Perkin Elmer Sigma 2000 chromatograph with a 3600 Data Station using an Analabs 1/8" x 6' stainless steel Spherocarb column (carbon molecular sieves) and a flame ionization detector. Gas chromatography/mass spectrometry (GC/MS) data were obtained on a Hewlett Packard 5985 instrument equipped with a 60-m DB5 capillary column. Thermogravimetric analysis was performed under flowing oxygen using a DuPont 951 Thermogravimetric Analyzer connected to a DuPont 1090 Thermal Analyzer controller. Electron paramagnetic resonance (EPR) spectra were recorded with a Varian E-109 spectrometer using powder samples in 3-mm inner-diameter quartz tubes. Spectra were recorded with 0.1 mT modulation amplitude and 0.88 mW microwave power at -196°C . The spectrometer frequency was near 9.217 GHz and spectra were calibrated with 1,1-diphenyl-2-picrylhydrazyl (DPPH), whose g value was taken as 2.0037.²²

Preparation of ZnS . Diethylzinc (15.2 g, 0.123 mol) was transferred to a 100-mL Schlenk flask and diluted to 62 mL with toluene to obtain a 2 M solution. Toluene (200 mL) was added to a septum-capped 500-mL Schlenk flask immersed in a bath maintained at -20 to -30°C . H_2S was purged through the cooled toluene using an 18-gauge stainless steel needle. The toluene solution was deemed saturated with H_2S when mineral oil bubblers on the inlet and outlet sides of the flask bubbled at the same rate. With continued H_2S flow and rapid magnetic stirring of the H_2S -saturated toluene solution, the diethylzinc solution was added via a 22-gauge cannula

submerged in both solutions over a period of 2 h. A faint bluish tint was observed for an instant and accompanied by precipitation immediately after the diethylzinc addition was started. After addition was complete, the H_2S purge was stopped and the reaction flask warmed to room temperature to allow excess H_2S to escape. The resultant mixture sat overnight before workup. The white solid was collected by filtration in a Schlenk frit and washed with 25 mL of toluene. The solid was dried overnight at 10^{-3} torr, giving a crude yield of 13.5 g. The solid was transferred to a 250 mL flask with a 24/40 inner joint (to minimize stopcock grease contamination) and heated at 10^{-4} torr for 16 h at 140°C . The yield was 12.2 g (101.5% of theoretical yield for ZnS). **Caution:** Considerable quantities of H_2S are evolved in the drying process.

Gas Phase Reaction of Et_2Zn and H_2S . A 200 mL Schlenk flask was purged with H_2S through an 18-gauge needle. Argon was purged through 0.9 g of Et_2Zn in a 10 mL Schlenk flask using a 20 gauge needle with the gas exiting through a 22-gauge cannula to the reaction flask. The gaseous argon/ Et_2Zn mixed with the gaseous H_2S in the 200-mL Schlenk flask. The relative purge rates of H_2S and argon/ Et_2Zn was maintained at 1.2 to 1 over a period of 100 min as a white powder collected in the reaction flask.

Acid Hydrolysis of ZnS with Analysis of Released Alkane Gases by Gas Chromatography. In a glove box 0.20 g of ZnS was weighed into a 53-mL Schlenk flask that contained a magnetic stirbar; the flask was sealed with a Subaseal septum. After evacuating the flask, 5 mL of 4 N HCl were added via a gas-tight syringe and the mixture stirred for 10 min. The gas phase was sampled by inserting a syringe with a valve through the septum, taking a 1 mL sample, closing the valve on the syringe, compressing the sample to 0.5 mL, opening the valve on the syringe momentarily to reduce the pressure in the syringe to 1 atm, and injecting the sample into the gas chromatograph. The molar ratio of alkane to zinc was determined as follows. The moles of H_2S produced are calculated assuming the sample is pure ZnS . Application of the ideal gas law and Henry's law (solubility of H_2S is 0.10 M for 1 atm pressure of H_2S) gives the

distribution of H_2S in the gas phase and in solution, eq. 1. V_s is the solution volume in L and V_g is the gas volume.

$$\frac{(V_s) (0.10 \text{ M}) (P_{\text{H}_2\text{S}} (\text{atm}))}{1 \text{ atm}} + \frac{(V_g) (P_{\text{H}_2\text{S}} (\text{atm}))}{RT} = \text{mol H}_2\text{S} \approx \text{mol Zn} \quad (1)$$

The gas chromatography data gives the ratio of the partial pressure of alkane to total pressure in the flask and, for small amounts of alkane, this ratio is approximated by $(P_{\text{alkane}})/(P_{\text{H}_2\text{S}} + P_{\text{H}_2\text{O}})$. The desired quantity $(\text{mol alkane})/(\text{mol Zn})$ is then related to the experimental data as follows:

$$\frac{\text{mol alkane}}{\text{mol Zn}} \approx \frac{\text{mol alkane}}{\text{mol H}_2\text{S}} = \frac{P_{\text{alkane}}}{P'_{\text{H}_2\text{S}}} = \frac{P_{\text{alkane}}}{P_{\text{H}_2\text{S}} + P_{\text{H}_2\text{O}}} \times \frac{P_{\text{H}_2\text{S}} + P_{\text{H}_2\text{O}}}{P'_{\text{H}_2\text{S}}} \quad (2)$$

where $P'_{\text{H}_2\text{S}}$ is the hypothetical pressure of H_2S if none of the H_2S dissolves in solution. (It is assumed that none of the alkane liberated by hydrolysis dissolves in solution.) $P'_{\text{H}_2\text{S}}$ is calculated using the ideal gas law (volume = 0.048 L), $P_{\text{H}_2\text{S}}$ is calculated from eq. 1 (solution volume = 0.005 L, gas volume = 0.048 L, $T = 298 \text{ K}$), and $P_{\text{H}_2\text{O}}$ is taken to be 20 torr. For a 0.20 g sample of ZnS the calculated values are $P_{\text{H}_2\text{S}} = 634 \text{ torr}$, $P'_{\text{H}_2\text{S}} = 794 \text{ torr}$, and the correction factor, $(P_{\text{H}_2\text{S}} + P_{\text{H}_2\text{O}})/P'_{\text{H}_2\text{S}} = 0.82$.

Acid Hydrolysis of ZnS for Characterization of Organic Impurities by NMR Spectroscopy. In a glove box 0.15 g of ZnS was weighed into a vial containing a magnetic stirbar. In a fume hood 1 mL of C_6D_6 was added to the vial and then a quantity of 38% DCl in D_2O sufficient to dissolve the ZnS (typically 0.5 to 1.0 mL) was added dropwise with magnetic stirring. NMR spectra were taken of the benzene and aqueous layers (100 to 200 scans were averaged). One μL of acetone was added to the benzene sample and 1.0 μL of methanol was added to the aqueous sample as integration standards. The estimated limit of detection of organic

molecules such as tetrahydrofuran and ethanol is 10^{-4} mol per mol of Zn. The estimated accuracy is $\pm 30\%$.

Ozone Treatment of ZnS. ZnS powder was first dried by heating at 200°C for 27 h at 10^{-4} torr. The dried yellowish white powder (5.27 g) was transferred to the ozonolysis frit which was then purged with O_2 at 85 mL/min for 1 h. The powder formed a layer about 1 mm thick on the frit. Ozonolysis was conducted by intermittently applying power to the transformer for O_3 generation while O_2 was continuously purged through the O_3 generator and sample frit. Intermittent exposure was required because continuous exposure of freshly prepared ZnS to O_3 led to a runaway reaction in which the solid glowed red hot and was converted to ZnO. The ozone generator was on for a total of 10 min over a period of 96 min. The fraction of time that the generator was on was gradually increased during the experiment. It was on for 2 s of the first min, then 3 s of the second min, 4 s of the third min, and 5 s of each of the next 5 min. During the last 3 min of generator time, it was on for 15 s of each min. The powder was noticeably yellow in spots after 20 s of ozone treatment. The frit was disconnected and shaken after every 2 min of generator time to obtain a more uniform exposure of the powder to O_3 . The sample was purged with O_2 for 4 min before and after each mixing step. The powder after treatment was yellow and weighed 5.36 g (1.7% weight gain).

Oxygen Treatment of ZnS. ZnS powder was dried by heating under vacuum at 200°C for 27 h followed by gradual heating to 300°C over a period of 4 h and then maintaining at 300°C for 1 h at 10^{-4} torr. The dried, pale yellow powder (4.53 g) was transferred to a 26 x 122 mm quartz boat which was purged in a quartz tube for 30 min with O_2 , heated to 400°C over 40 min, and maintained at 400°C for 30 min. After cooling the powder was light tan and weighed 4.60 g (1.5% weight gain).

Vacuum Heat Treatment of O₂- and O₃-Treated ZnS. O₂-treated ZnS (4.18 g) was transferred to a quartz flask and evacuated for 1 h at 25°C at 1×10^{-5} torr. The sample was then heated to 800°C over 6 h and held at that temperature for 40 min (3×10^{-5} torr). A metallic golden brown film formed on the neck of the flask 3 to 10 cm above the furnace during heating at 760 to 800°C. After cooling to 25°C the light yellow powder weighed 4.08 g (2.4% weight loss). Similar treatment of O₃-treated ZnS led to similar film formation and a white solid product with 3.5% weight loss.

Hot Isostatic Pressing (HIPping) of ZnS Powders. In a glove box under dry nitrogen approximately 4 g each of the O₃ and O₂-treated powders were transferred to rubber containers for cold isostatic pressing at 138 MPa (20,000 psi). The powders had not been exposed to air at any stage of treatment. The cold pressed specimens were then placed in Pyrex tubes and evacuated to approximately 5×10^{-7} torr at 200°C. The evacuated specimens were briefly heated to approximately 750°C to slump the glass onto their surfaces, eliminating unsupported glass that might crack during the subsequent HIP treatment, and then sealed. The O₂-treated specimen was inadvertently exposed to the laboratory atmosphere for a few minutes when a leak developed during the sealing operation. At the time, the powder was no warmer than 100°C. It was lightly reground to a powder using a mortar and pestle in the glove box, repressed, and encapsulated. The encapsulated specimens were heated to 775°C under an applied pressure of approximately 0.3 MPa (50 psi), held at 775°C for 15 minutes to soften the glass, and pressurized to 100 MPa over 45 min. The treatment was continued for 1 h. Both specimens were fractured when removed from their encapsulants. The largest fragments of each (approximately 2 mm thick) were mounted in epoxy for hardness measurements and microscopy. A specimen of standard Raytran™ ZnS of similar thickness was also mounted and polished to provide a reference standard for hardness and fracture toughness comparisons.

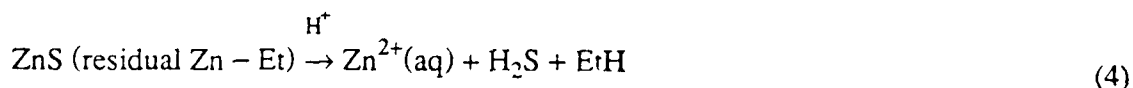
RESULTS AND DISCUSSION

Synthesis of ZnS Powder. When a diethylzinc/heptane solution was purged with H₂S at 0°C a fine white precipitate formed immediately and gas evolution occurred:



The outlet of the needle, through which the H₂S was purged, plugged frequently during the reaction due to accumulation of the solid product. This problem was avoided by changing the method of addition such that the Et₂Zn solution was added to solvent which was already saturated with H₂S at -20°C. After drying the solid product at 140°C under vacuum, the mass of product was 101.5% of that calculated for pure ZnS based on eq. 1. X-ray diffraction in Fig. 1A indicated that the sample contained poorly crystalline ZnS, mostly in the cubic phase. Scanning and transmission electron micrographs in Fig. 2 showed that the powder consisted of agglomerated 0.1-μm-sized particles that are in turn composed of fragments with dimensions on the order of 10 nm. Average crystallite sizes calculated from X-ray line widths by the Scherrer equation²³ are dependent on the reaction temperature: 3 nm for -35°C, 5 nm for 25°C, and 13 nm for 100°C.

In order to determine the extent of reaction of Et₂Zn and H₂S, the solid product was hydrolyzed with hydrochloric acid and the ethane produced was measured by gas chromatography²⁴ (eq. 4).



Results in Table I show that the procedure involving Et₂Zn/toluene addition to an H₂S saturated toluene solution gave much less residual zinc-ethyl groups than the procedure of purging H₂S

through Et_2Zn /heptane. The change in solvent was not responsible for the large reduction in residual zinc-ethyl groups, as preliminary experiments indicated only about a twofold increase in residual zinc-ethyl groups when heptane was used instead of toluene. Other factors favoring more complete reaction are dilution of the Et_2Zn , slow addition of Et_2Zn to H_2S /toluene, and low reaction temperature. We conclude that the critical factor is maintaining a large excess of H_2S during the reaction. Lowering the temperature gives a larger $\text{H}_2\text{S}:\text{Et}_2\text{Zn}$ ratio due to the increased solubility of H_2S .

Table I also shows that $t\text{-Bu}_2\text{Zn}$ reacts more completely than Et_2Zn with H_2S at 25°C . Me_2Zn appears to have about the same extent of reaction as Et_2Zn at 25°C . However, upon examination of the relative amounts of ethane and methane for each entry in Table I, one finds that the methane amount is higher than expected based on the 0.3% methyl group content of the Et_2Zn reagent. The difference is most pronounced for the -78°C case where the observed methane:ethane ratio of 12 is 4000 times higher than the fractional amount of methyl groups in the dialkylzinc reagent. Thus, it appears that Et_2Zn is more reactive than Me_2Zn and, based on the trend in the methane:ethane ratio with reaction temperature, that the activation energy is less for the Et_2Zn reaction. The observed order of reactivity is thus inversely related to the order of thermal stability²⁵ of the dialkylzinc compounds which is $\text{Me}_2\text{Zn} > \text{Et}_2\text{Zn} > t\text{-Bu}_2\text{Zn}$.

The gas phase reaction of Et_2Zn and H_2S gave a product with considerable residual zinc-ethyl groups (last entry in Table I). Interestingly, the product contains roughly equal amounts of cubic and hexagonal ZnS according to the X-ray powder diffraction pattern in Fig. 1B. The cubic phase is thermodynamically more stable at low temperature while the hexagonal phase is more stable above 1020°C .²⁶ This phenomenon of a gas phase reaction tending to produce a metastable phase has been noted elsewhere.²⁷

Characterization of Impurities in ZnS. In addition to residual zinc-alkyl groups, other organic and inorganic impurities in the ZnS powder have been identified using infrared and NMR spectroscopies. The diffuse reflectance Fourier transform infrared (FTIR) spectrum of ZnS powder dried at 200°C exhibits peaks at 2440 and 2530 cm^{-1} assigned to S-H vibrations from Zn-SH groups (Fig. 3A). These peaks are diminished upon further heating of the sample under vacuum during which H_2S evolves. We believe that the S-H groups account for the slightly greater than theoretical yield of ZnS and that the product dried at 140°C, therefore, has the approximate composition $\text{ZnS}_{0.95}(\text{SH})_{0.1}$. The diffuse reflectance infrared spectrum in Fig. 3A also exhibits very weak peaks in the region 2850 to 3000 cm^{-1} assigned to aliphatic organic groups. The intense peaks at 3350 (very broad) and 1610 cm^{-1} are assigned to water that is presumably adsorbed while handling the powder in air to obtain the infrared spectrum. The powder is otherwise synthesized and maintained in a strictly anhydrous atmosphere.

Hydrolysis of ZnS followed by NMR analysis was used to identify organic impurities. Two impurities were observed in the benzene layer. Toluene (CH_3 group at δ 2.107) was present at 200 ppm (2×10^{-4} mol toluene per mol Zn) in a sample dried under vacuum at 200°C for 27 h. The other impurity exhibited a doublet at δ 1.077, 0.995 and was identified as isopropylthiol by both the addition of authentic reagent and homonuclear decoupling at δ 2.74. The amount of i-PrSH observed corresponded to 400 ppm. The i-PrSH was traced to the H_2S reagent by NMR analysis of a C_6D_6 sample purged with H_2S for 20 min at 8°C. After further heating of the ZnS under vacuum at 300°C for 1 h, hydrolysis/NMR analysis gave 100 ppm of toluene while no i-PrSH was detected (≤ 50 ppm i-PrSH).

An earlier ZnS preparation contained tetrahydrofuran (THF) impurity (multiplets at δ 3.56, 1.42 in the benzene layer from hydrolysis/NMR corresponding to 3200 ppm THF), probably due to contamination of the toluene solvent used in the synthesis. The sample had been dried under vacuum first at 100°C for 19 h and then at 125°C for 2 h. After heating the sample further at 137°C

under vacuum for 17 h, hydrolysis/NMR showed 1600 ppm of THF in the benzene layer and 1000 ppm of tetrahydrothiophene (THT) (multiplets at δ 2.54, 1.46). Identification of THT was confirmed by GC/MS of a pentane solution obtained by hydrolysis of ZnS with concentrated HCl in the presence of pentane. Further heating of the ZnS sample at 159°C for 15 h gave a material that produced 300 ppm of THF and 2800 ppm of THT in the benzene layer after hydrolysis. Thus, it is apparent that THF is not removed from ZnS by heating under vacuum but rather converted to THT. It is known that THF can be converted to THT by reaction with H₂S at 400°C catalyzed by Al₂O₃.²⁸ The ZnS powder is active in promoting the THF to THT conversion.

Pyrolysis was used to evaluate carbonaceous impurities in the ZnS samples. Organic impurities imparted a gray color to the ZnS powder upon heating for 20 s over a blue propane-O₂ flame in a sealed, evacuated quartz tube. This procedure provides a quick qualitative test for organic impurities and was especially useful in evaluating the treatment procedures described in the following section. Zinc metal is ruled out as a possible source of the gray color for three reasons. First, dissolution of the ZnS in acid gave a gray insoluble material. Second, acid hydrolysis of a gray ZnS sample that had been heated at 800°C for 2 h in an evacuated sealed tube released ≤ 10 ppm of H₂. Third, the temperature of most pyrolyses was $\geq 1000^\circ\text{C}$ which is sufficient to volatilize zinc (b.p. 907°C). (X-ray diffraction indicated that a considerable amount of the sample had been converted from cubic ZnS to hexagonal ZnS, whose transition occurs at 1020°C.²⁶)

ZnS samples dried at 200 and 300°C that contained i-PrSH and/or toluene impurities both took on a slight gray tint upon pyrolysis. The sample dried at 300°C had a slightly lighter tint, consistent with its reduced organic content determined by hydrolysis/NMR analysis. We attempted to remove all organic impurities from ZnS by heating to higher temperatures under vacuum. A sample initially dried at 200°C was heated over a period of 17 h to reach 800°C and held at that

temperature for 1 h. After cooling to room temperature the sample was light gray. Thus, carbonaceous impurities cannot be completely removed by heating under vacuum.

In another experiment we attempted to remove organic impurities by heating ZnS powder in the presence of H_2 . The powder, which had been previously dried at $140^\circ C$, was dispersed on a glass frit and H_2 passed through the sample while heating to $467^\circ C$ at $2^\circ C/min$. After cooling to $25^\circ C$ the powder was cream-colored. Upon subjecting this powder to the pyrolysis procedure, we obtained a light gray powder that was similar in appearance to the powder heated under vacuum at $800^\circ C$. Again, we concluded that carbonaceous impurities remained in the ZnS powder.

Oxidative Treatments. A patent claims an oxidative purification procedure for ZnS powder that eliminates organic matter and free sulfur and also reduces sulfate concentration.²⁹ The procedure involves sequential heating of the powder under air or oxygen at $460^\circ C$, H_2S at $480^\circ C$, and H_2 at $500^\circ C$. Before carrying out this procedure, we determined the thermal behavior of our ZnS powder under oxygen by thermogravimetric analysis. A 17.2 mg sample was heated from 25 to $475^\circ C$ at $50^\circ C/min$ and then to $800^\circ C$ at $10^\circ C/min$. The sample lost 1% of its weight while heating to $350^\circ C$, then gained 1% in weight while heating to $500^\circ C$, and finally lost 17% of its weight while heating to $640^\circ C$. The majority of the weight loss occurred in the range 620 to $640^\circ C$. The weight changes are likely due to sequential dehydration, partial conversion to $ZnSO_4$ (about 1 mol %), and then essentially quantitative conversion to ZnO. When the patented procedure was applied to our powder, we encountered two problems. First, the powder after treatment still contained some organic impurity as evidenced by weak C-H stretching bands observed in diffuse reflectance IR spectra. However, this impurity probably results from impurities in the H_2S reagent, rather than incomplete oxidation of the original organic impurity. (We base this on separate experiments that show that organic impurities can be introduced by treatment with H_2S contaminated with $i\text{-PrSH}$.) The second and more serious problem encountered was particle growth and necking. Particles grew to as much as $1\text{ }\mu m$ in their longest

dimension and considerable fusing of particles occurred. Particle growth was traced to the early stages of the initial oxidation step and may occur concomitant with the oxidation of the organic impurities. Since retention of the small particle size was critical for producing a fine-grained ZnS ceramic, we decided to investigate O_3 as an alternative oxidizing agent.

O_3 (1 mol % in O_2) was passed through ZnS powder dispersed on a glass frit. The powder was treated with ozone for various lengths of time and then subjected to pyrolysis as a qualitative test for residual unoxidized organic material. The O_3/O_2 mixture was effective at 25°C in oxidizing the organic impurities. After pyrolysis the samples appeared white or slightly yellow, and no gray color was evident. Furthermore, no particle growth was evident by SEM. When the sample size was increased from 0.1 to 0.5 g on a 20 mm frit, runaway oxidation tended to occur in which the sample reached red heat and was converted to ZnO identified by X-ray powder diffraction. The runaway oxidation could be avoided by intermittently operating the O_3 generator, thereby reducing the ozone concentration.

Additional experiments using O_2 to oxidize the organic impurities were conducted to optimize this procedure for comparison to the ozone results. ZnS samples heated for 20 min under flowing O_2 at 450 or 400°C gave cream-white solids with the 400°C sample being slightly darker. Pyrolysis of the samples gave a yellow powder for the 450°C sample and a light yellow powder for the 400°C sample. Thus, the 400°C O_2 treatment appears to be sufficient to oxidize the organics.

Both the O_3 treatment at 23°C and the O_2 treatment at 400°C were conducted on a 5 g scale to allow for subsequent processing studies. Diffuse reflectance FTIR spectra of the powders before and after the oxidative treatment (Fig. 3A and B and Fig. 4A and B) show that the major change is the appearance of a new broad peak at approximately 1120 cm^{-1} assigned to ZnSO_4 . The S-H peaks at 2440 and 2530 cm^{-1} diminish as a result of the ozone treatment and are eliminated in the O_2 -treated sample. The O_3 - and O_2 -treated samples increased in weight by 1.7 and 1.5%,

respectively, during treatment. If the major process occurring is the conversion of ZnS to ZnSO₄, the weight increases correspond to 2.6 and 2.2 mol % conversion to ZnSO₄, respectively, for the O₃ and O₂-treated samples. No impurity phases were detected by powder X-ray diffraction in the treated powders. However, by subjecting an ozonized sample to the pyrolysis procedure, the diffraction lines became much sharper and two barely discernible peaks were observed at positions corresponding to the 100% lines of ZnSO₄ and ZnO. Zinc sulfate is the expected major product of the slow reaction of oxygen with ZnS at temperatures $\leq 500^{\circ}\text{C}$, while at higher temperatures ZnO predominates.³⁰ The chemistry of the O₃ and O₂ treatments appears to be quite similar, with the greater reactivity of O₃ allowing its use at lower temperatures. Thus, we expect that O₃ may find application as an oxidizing agent in other systems where elevated temperatures need to be avoided to control particle growth or because of thermal instability.³¹

Post-Oxidative Treatments. Although the organic impurities were removed by the oxidative treatment, a new problem was created in the form of the sulfate impurity which has a strong and undesirable infrared absorption. Ultimately, we chose to eliminate the sulfate impurity by slow heating under vacuum causing decomposition of ZnSO₄ to ZnO, but we came to this point by a rather circuitous route. In exploratory experiments on O₃-treated ZnS, we attempted to reduce ZnSO₄ to ZnS by treating the powder for one hour at 480 to 500°C with either H₂S, H₂S followed by H₂, H₂ and sulfur, or H₂ alone. In all cases a small amount of sulfate was still detectable by IR spectroscopy and the powder turned gray during the treatment. We were puzzled by the gray coloration, but had noticed that when ozonized samples were subjected to the pyrolysis procedure they also typically turned gray under mild heating and then became light yellow upon heating to higher temperatures. We then studied the behavior of O₃-treated ZnS heated under flowing Ar and found that samples typically turned gray when heated to 250 to 300°C, then yellow at 500 to 650°C, and remained yellow when cooled to 25°C. Samples that were heated to $\geq 650^{\circ}\text{C}$ showed no discernible IR peaks for sulfate. The ZnSO₄ probably decomposes via eq. 5.^{30c,32} The origin

of the gray color remains unknown, but may arise from metastable species generated in the O₃ treatment.



At this point we decided to pursue heating under vacuum to eliminate the sulfate impurity. Heating to 700°C was sufficient to remove sulfate but, surprisingly, IR spectra showed for some samples a sizeable peak for CO₂. The peak appeared as a barely resolved doublet at 2353 and 2340 cm⁻¹ and contained weak rotational fine structure indicative of gaseous CO₂ trapped within the solid. This result indicates that while ozone is effective at oxidizing organic material the oxidized carbon species are not necessarily removed from the solid. We speculate that carboxyl or carboxylate groups may be formed during the ozone treatment and that subsequent heating releases CO₂.

The final treatment adopted was slow heating of the oxidized samples to 800°C under vacuum. This temperature was chosen because it was close to the expected HIPping temperature and also would allow for minimal sulfate and CO₂ impurity. We recognized that ZnO would be a remaining impurity but hoped that it would not interfere with the primary objectives of producing fine-grained carbon-free ZnS ceramic suitable for mechanical testing. Figure 5 shows SEM of ZnS powder before and after oxidative treatments. Note that the particle size is essentially unaffected by the procedure involving O₃, with individual particles remaining 0.1 to 0.2 μm in size. The O₂-treated powder shows slight particle growth but considerable necking of particles which occurred during the 400°C O₂ exposure. The O₃- and O₂-treated samples experienced a weight loss during the final treatment of 3.5 and 2.4%, respectively. Pressure measurements show that the majority of the weight loss occurred while heating at 380 to 500°C for the O₃-treated sample and at 500 to 550°C for the O₂-treated sample. Diffuse reflectance FTIR spectra (Figs. 3C and 4C) show that the sulfate bands have been essentially eliminated along with the residual S-H bands of the O₃-treated sample. The spectrum of the O₃-treated sample contains weak bands at 3400 and 1620 cm⁻¹ due to

adsorbed water, 2350 cm^{-1} due to CO_2 , and 1220 cm^{-1} probably due to a sulfate species.³³ Both final diffuse reflectance spectra also exhibit gradually rising baselines toward longer wavelengths. The final powders are much less hygroscopic than the starting powder, presumably from a reduction in surface area. The presence of ZnO in the powders after treatment is confirmed by X-ray powder diffraction patterns in Fig. 6. Weak peaks at $d = 2.81$, 2.60 , and $2.47\text{ \AA}$ in the O_2 -treated sample correspond to the three most intense lines of ZnO. A very weak peak for the 100% line of ZnO may also be present in the O_3 -treated sample. The rest of the diffraction lines correspond to β -ZnS and a small amount of α -ZnS ($d = 3.29$ and $2.92\text{ \AA}$). Note that these lines are much sharper than those of the untreated powder (Fig. 1A), a result of the 800°C treatment.

We believe that the chemistry occurring during the final 800°C treatment of the O_2 -treated sample is mainly decomposition of ZnSO_4 according to eq. 5. Based on the observed weight loss, the calculated amount of ZnO produced is $3.8\text{ mol \%}$ (originating from $2.9\text{ mol \% ZnSO}_4$). This compares to $2.2\text{ mol \% ZnSO}_4$ calculated from weight gain during the O_2 treatment. Although the O_3 -treated sample experienced a larger weight loss when heated to 800°C , it apparently formed less ZnO according to the X-ray data.

During the final heating step, a metallic golden brown film formed on the neck of the flask outside the furnace. Similar films also formed when powders were pyrolyzed over a burner. Analysis of the film by Auger electron spectroscopy gave a relative atomic composition of $63\%\text{ Zn}$, $21\%\text{ O}$, and $16\%\text{ S}$. The Zn-rich nature of the film is consistent with eq. 6, an endothermic process that reportedly occurs at 800°C .³⁴



Reaction 6 proceeds very slowly at 800°C, as indicated by the relatively low dynamic pressure (3×10^{-5} torr) observed while heating the O₂-treated sample at 800°C. However, at somewhat higher temperature, this process might be suitable for removing ZnO impurity from ZnS powders.

Impurities and defects in ZnS powders at various stages of treatment were observed by EPR spectroscopy. ZnS precipitated from the diethylzinc/H₂S reaction has very weak EPR signals near $g = 2.00$. Upon drying at 200 or 300°C, the signals in the top two traces of Fig. 7 are seen. The origin of these signals is not known. After oxidative treatment with either O₃ or O₂ (Fig. 7, middle traces), stronger EPR signals are observed. (Note that the middle spectra would be stronger if recorded at the same gain as the upper spectra.) The unknown feature with a peak near $g = 2.014$ in the upper spectra is still present in the lower spectra. Most of the new strong signals that appear in the middle spectra are consistent with the formation of SO₂⁻ radicals after oxidation. In the left spectrum the signals appear at $g = 2.010$ and 2.002 . In the right spectrum they appear at $g = 2.008$ and 2.003 (with a barely discernible shoulder at $g = 2.002$.) A similarly shaped set of signals is reported for SO₂⁻ on ZnS, with g values of 2.007 and 2.003.³⁵ Similar g values and roughly similar spectra have been reported for SO₂⁻ adsorbed on V₂O₅,³⁶ on CaO,³⁷ and on MgO.³⁸ Shoulders near $g = 2.024$ and 2.018 in the central spectra are unidentified. After heating each oxidized powder to 800°C in vacuum, most of the EPR signals disappear and a new unidentified signal at $g = 1.956$ appears (Fig. 7, bottom traces). The vacuum heated samples also exhibit six sharp lines due to Mn²⁺ (only some are shown in Fig. 7 and marked with asterisks). The observed Mn²⁺ hyperfine coupling in these samples, 6.84 mT, is in excellent agreement with published values for Mn²⁺ in single crystal cubic ZnS.^{39,40} The Mn²⁺ signals must be too broad to see in the earlier samples because they are not crystalline. Very weak peaks at $g = 2.003$ in the bottom traces are probably F centers (a single electron in a sulfur vacancy).^{41,42}

Processing of ZnS Powders. The O₃ and O₂ treated ZnS powders were densified by HIPping at 775°C. The temperature was chosen based on earlier results using an untreated powder

estimated to contain about 1 mol % organic carbon impurity by hydrolysis/NMR analysis. The three preliminary runs were conducted at 740, 775, and 850°C, and 100 MPa (15,000 psi) for 3 h. All three samples were black and opaque, attained full density within experimental error, and had a Knoop hardness close to twice that of Raytran™ ZnS. Upon densification the O₃-treated sample produced a fragmented uniform bright yellow compact that was marginally translucent in the thinnest slices. The yellow color may be due to Zn produced according to eq. 6. The oxygen-treated specimen had a mottled white to gray appearance and was opaque. The gray color is probably due to residual carbon. In support of this we find that dissolution of the ceramic in concentrated hydrochloric acid leaves dark gray insoluble matter. The non-uniform appearance may have been caused by the regrinding operation prior to the second encapsulation described in the Experimental section. The opacity of the samples is thought to be a result of the ZnO impurity. No porosity was apparent in either sample under an optical microscope. SEM of fracture surfaces does not show a well-developed crystalline microstructure. The micrographs in Fig. 8 were obtained from polished samples by etching for 10 s with concentrated HCl. The etch was a little too severe, especially for the oxygen treated sample, but a 6 M HCl etch failed to bring out any detail. The observed ZnS grains range from 0.1 to 0.5 µm in diameter. This compares to a grain size of typically 2 to 20 µm in Raytran™ ZnS prepared by chemical vapor deposition.

Hardness and fracture toughness values of the ZnS ceramics are summarized in Table II. The untreated ZnS sample contained about 1 mol % carbon. After hot pressing the sample was black and opaque. The powder-derived ceramics have about twice the hardness of chemically vapor deposited Raytran™ ZnS, but only half the fracture toughness. An attractive explanation for the low fracture toughness values is segregation of impurities to produce weakened grain boundaries. The O₃- and O₂-treated samples contain up to a few percent ZnO as a second phase impurity. The untreated sample contains about 1 mol % C. Other possible explanations for the low fracture toughness include a non-optimum choice of HIP parameters and residual stresses from the HIP treatment that are relieved by the propagating crack during the toughness measurements. Removal

of the second phase impurity would be necessary in order to obtain reliable data on relationships between grain size and hardness/toughness values for optimized HIP parameters. Possible procedures for removing the ZnO impurity are high temperature H₂S heat treatment of the powder using high purity H₂S or a vacuum heat treatment above 800°C to continue the process in reaction 6.

CONCLUSIONS

The reaction of diethylzinc with H₂S at -78 to 25°C produces reactive fine particles of zinc sulfide. This suggests that the synthetic method may be useful in general for preparing metal sulfide powders for applications in catalysis. An efficiency of conversion of the diethylzinc of $\geq 99.999\%$ was obtained by optimizing reaction conditions. However, residual organics in the form of the solvent toluene and i-PrSH from the H₂S reagent prevented conversion of the powder to a transparent ceramic. This problem might be remedied by using electronic grade H₂S reagent and switching to a non-hydrocarbon solvent such as carbon disulfide. Ozone was found to be an effective but not entirely selective oxidant at 25°C for organic impurities. The procedure may be more useful for organometallic-derived oxide materials where the need for selectivity should be less.

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Table I. Alkane Released by Acid Hydrolysis of ZnS Samples.

Preparation ^a		Alkane, ppm ^b	CH ₄ , ppm ^c
2 M	Et ₂ Zn/heptane, 0°C ^d	30,000	330
1 M	Et ₂ Zn, -20°C	10	1
Neat	Et ₂ Zn, -20°C	120	6
1 M	Et ₂ Zn, -20°C ^e	630	11
1 M	Et ₂ Zn, -78°C ^f	1	12
1 M	Et ₂ Zn, 25°C	270	6
0.3 M	t-Bu ₂ Zn, 25°C	7	-
0.4 M	Me ₂ Zn, 25°C	260	-
Gaseous	Et ₂ Zn, 25°C ^g	12,000	36

^aSolvent is toluene unless otherwise noted. Dialkyl zinc solution of indicated concentration added to saturated H₂S/toluene solution unless otherwise noted.

^b10⁶ x (mol of alkane from the primary zinc reagent) per mol of ZnS.

^cCH₄ from Me₂Zn impurity in Et₂Zn.

^dH₂S purged through Et₂Zn/heptane solution.

^eAddition rate increased by a factor of 13.

^fInitial [H₂S] was about 1.5 M.

^gArgon/Et₂Zn vapor mixed with H₂S.

Table II. Mechanical Properties of ZnS Samples.

ZnS Sample	Microhardness, GPa ^a	Toughness, MPa·m ^{1/2} ^b
O ₃ -treated	3.41 ±0.03	0.44 ±0.01
O ₂ -treated	3.22 ±0.12	0.47 ±0.08
Untreated ^c	3.72 ±0.13	0.54 ±0.02
Raytran ^{TMd}	1.69 ±0.04	0.96 ±0.04

^aObtained using a Vickers indenter on a Kentron Model AK205 Microhardness Tester.

^bObtained from indent and crack lengths using the approach in Ref. 43. Dimensions of 5 symmetrical indents for each specimen were averaged.

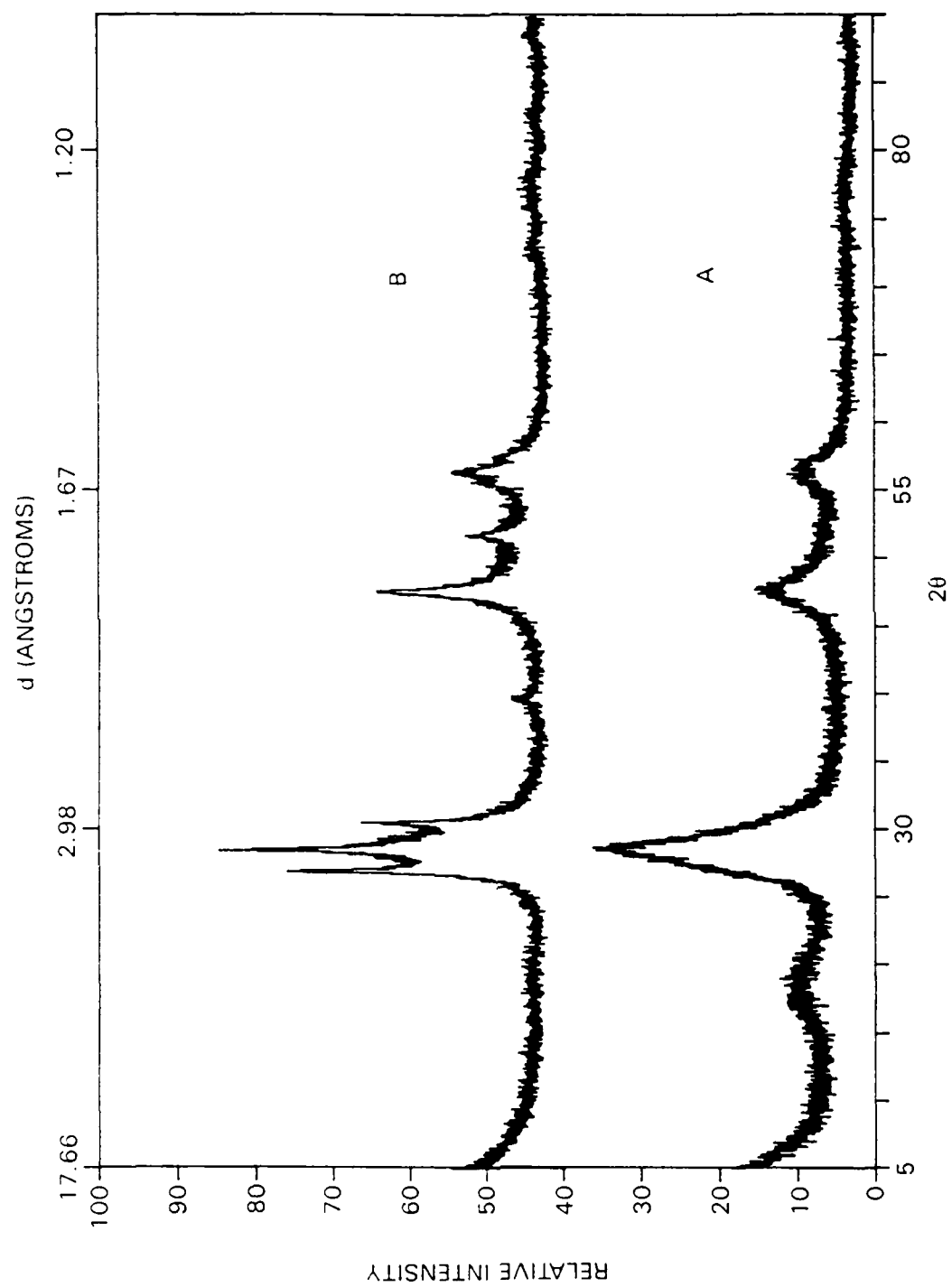
^cHot pressed at 830°C for 15 min at Coors Porcelain Co. Sample was polished on one side and evaluated as a free-standing piece.

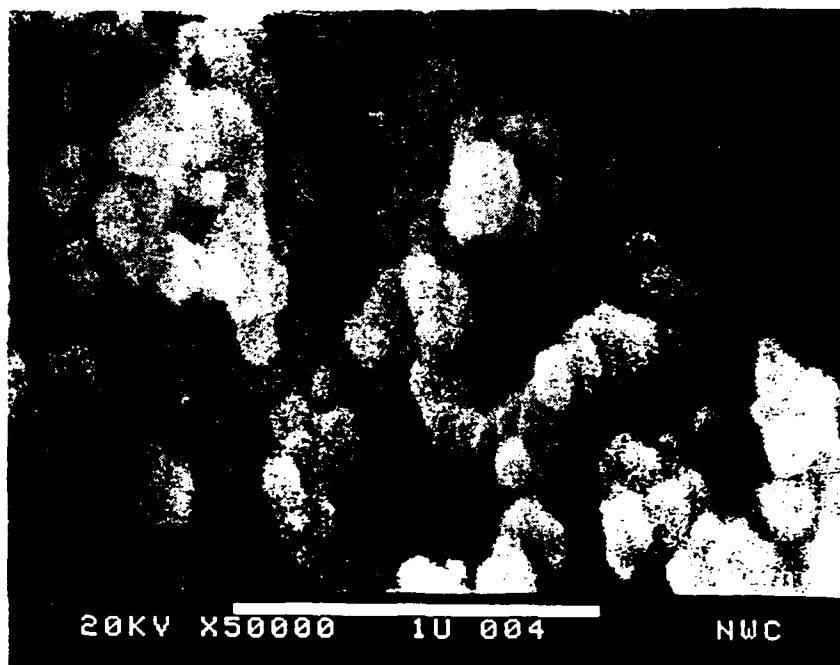
^dStandard Raytheon chemically vapor deposited material.

FIGURE CAPTIONS

- FIGURE 1. X-ray powder diffraction patterns of ZnS: (A) prepared in toluene solution at -20°C ; (B) prepared in the gas phase. The peak at $2\theta = 18^{\circ}$ is due to vaseline used to mount the samples.
- FIGURE 2. (A) Scanning electron micrograph of ZnS powder precipitated from toluene; sample was coated with Au to reduce charging effects. (B) Transmission electron micrograph.
- FIGURE 3. Diffuse reflectance FTIR spectra of ZnS powder: (A) dried at 200°C under vacuum; (B) then treated with O_3/O_2 at 25°C ; (C) then heated at 800°C under vacuum.
- FIGURE 4. Diffuse reflectance FTIR spectra of ZnS powder: (A) dried at 300°C under vacuum; (B) then treated with O_2 at 400°C ; (C) then heated at 800°C under vacuum.
- FIGURE 5. SEM of ZnS powder: (A) dried at 200°C under vacuum; (B) after O_3 treatment at 25°C and heating in vacuum at 800°C ; (C) after O_2 treatment at 400°C and heating in vacuum at 800°C .
- FIGURE 6. X-ray powder diffraction patterns of ZnS: (A) after O_3 treatment at 25°C and heating in vacuum at 800°C ; (B) after O_2 treatment at 400°C and heating in vacuum at 800°C .
- FIGURE 7. EPR spectra of ZnS powders at different stages of treatment involving O_3 (left) or O_2 (right). Relative spectrometer gain is shown at the left above each trace. Peaks marked by asterisks in the bottom trace are due to Mn^{2+} .

FIGURE 8. SEM of ZnS after HIPping and etching with HCl: (A) sample from powder treated with O₃; (B) sample from powder treated with O₂.





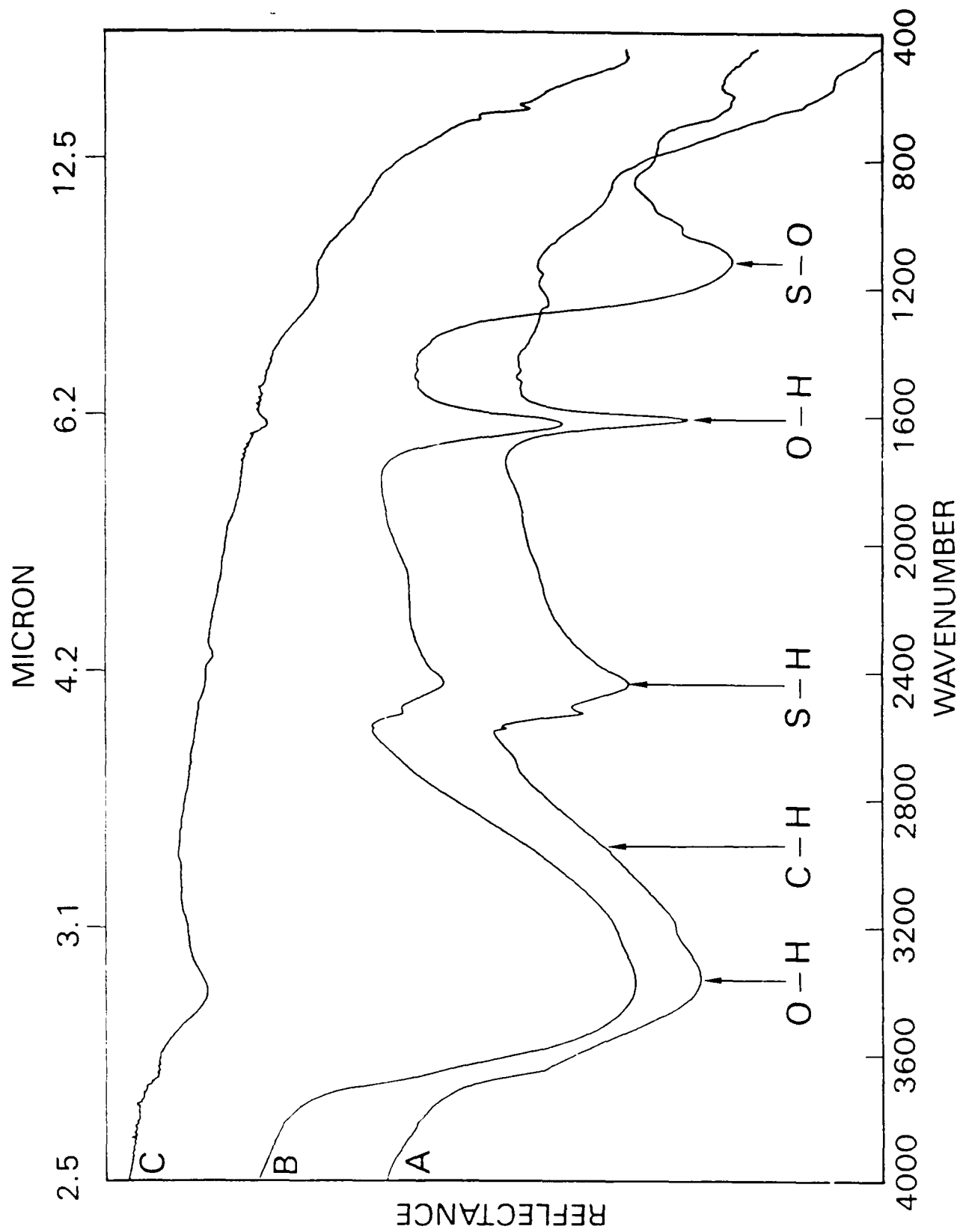
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Figure 2(A)



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Figure 2(B)

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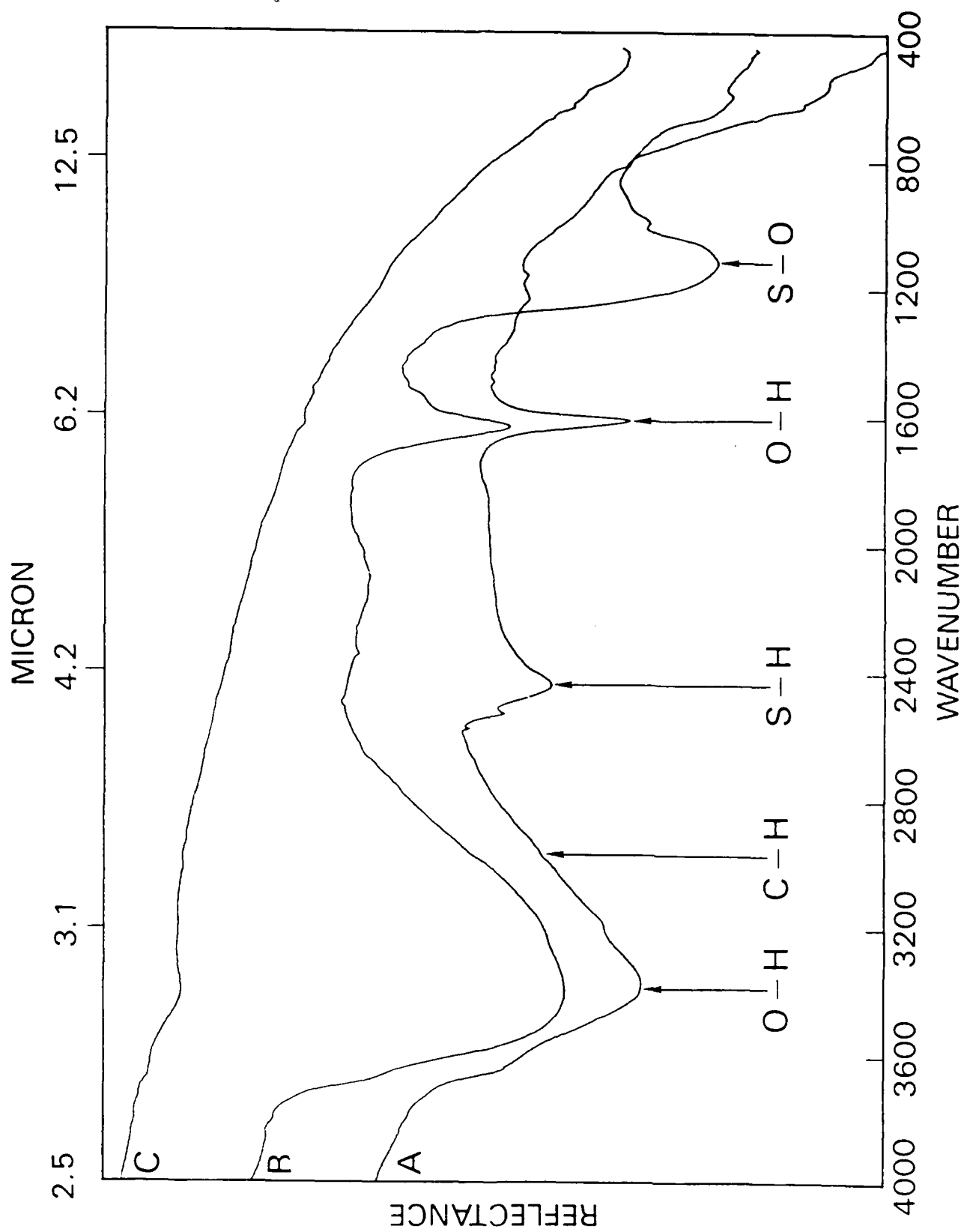


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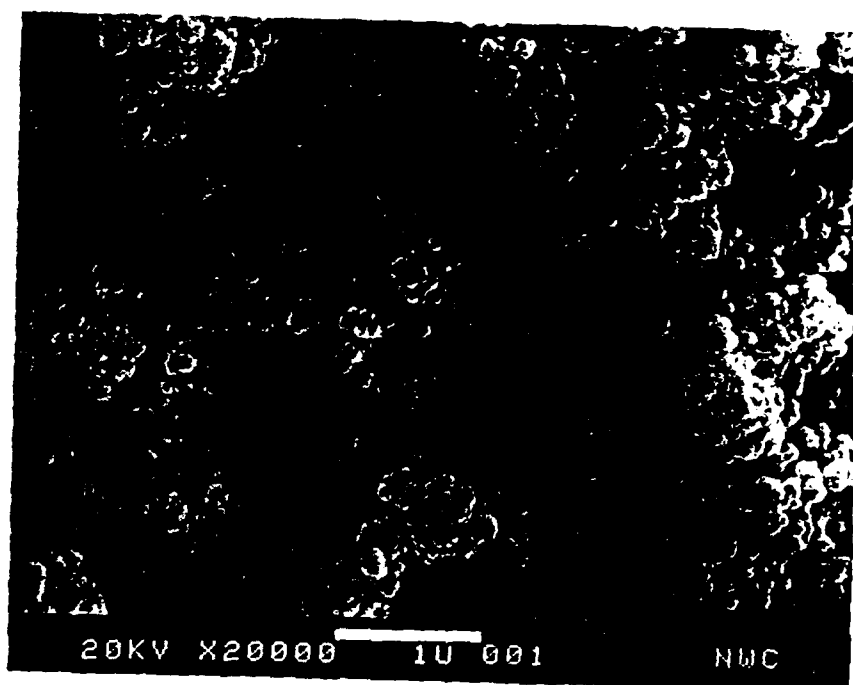
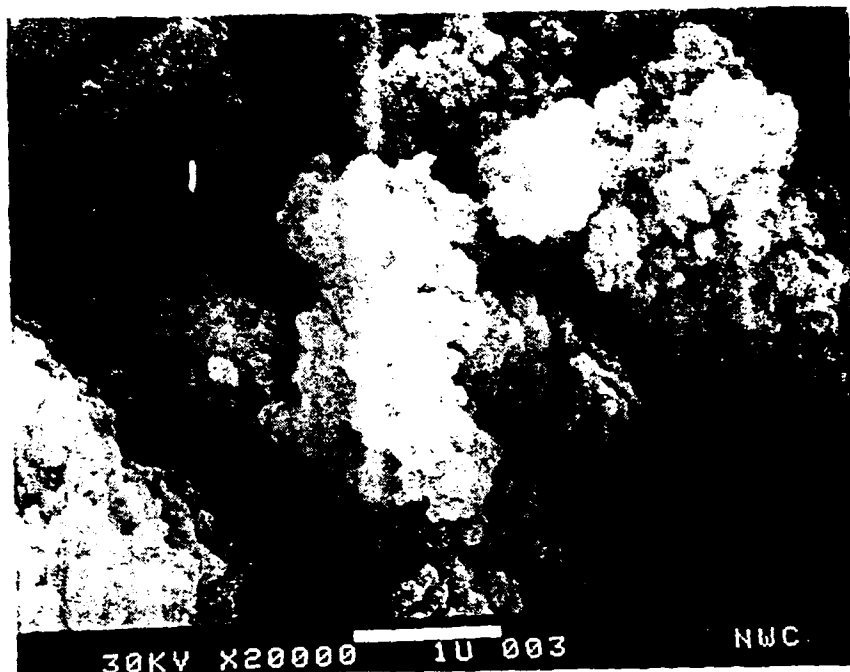
Figure 3

12 11 10 9 8 7 6 5 4 3 2 1

1
2



42 81 81 007



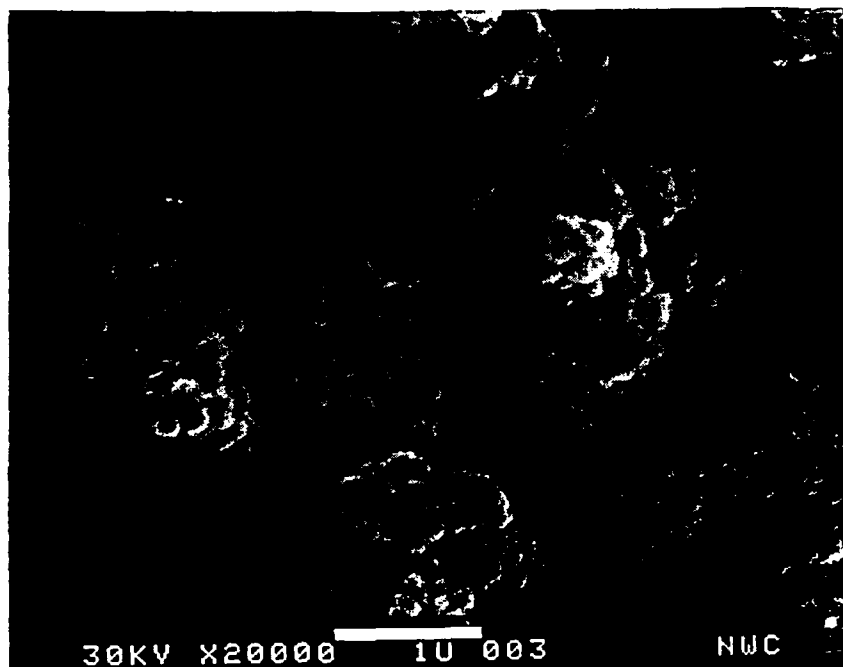
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Figure 5(A)

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Figure 5(B)

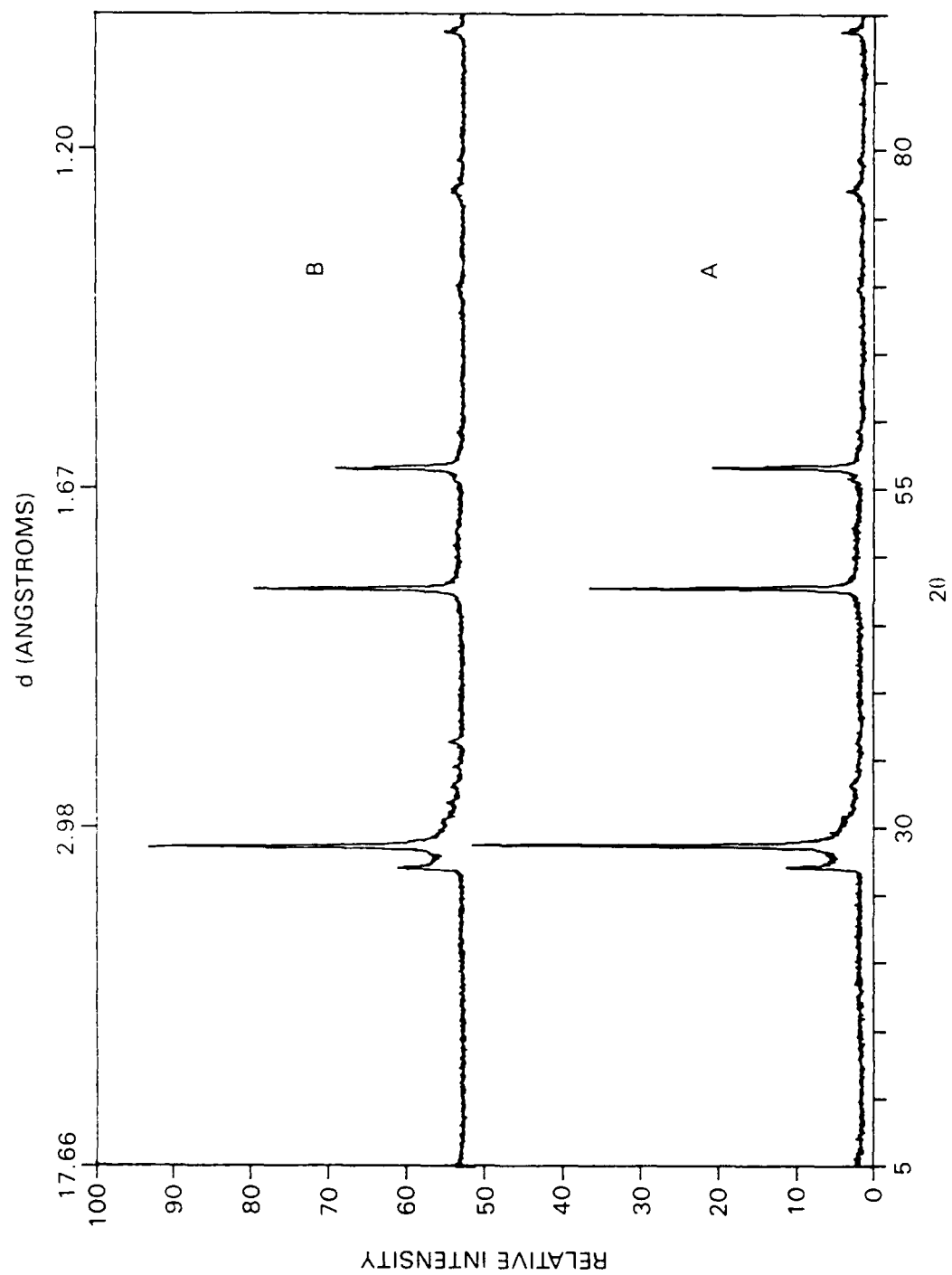
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Figure 5(C)

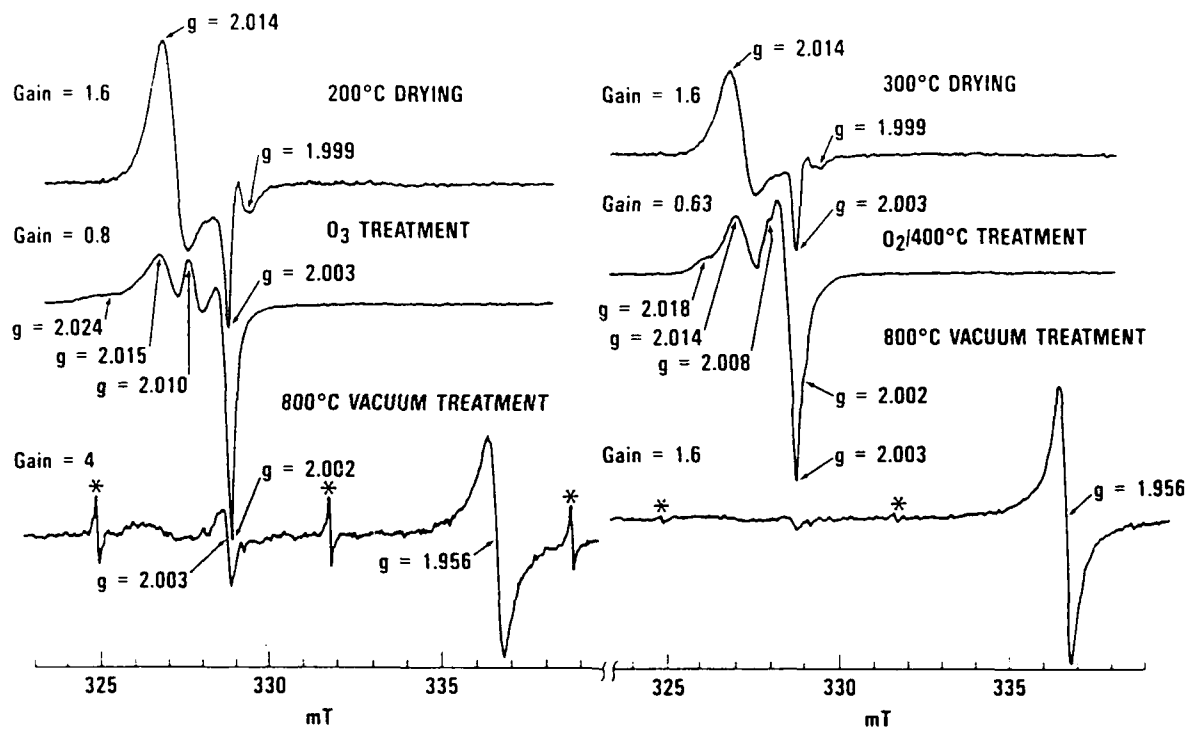
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Figure 6

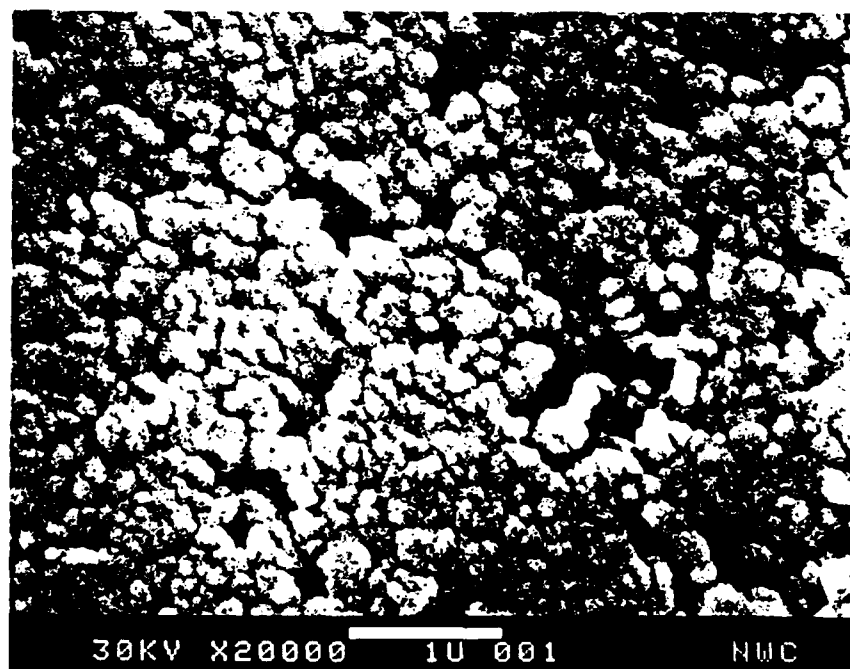
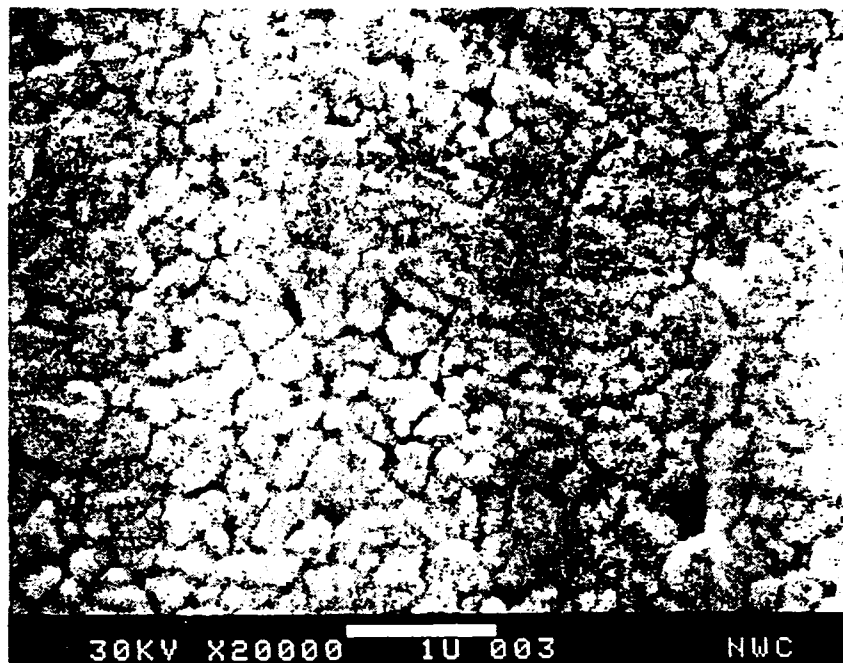
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Figure 7

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Figure 8(B)

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