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ZnS Doped by Electron Donating Organic Ligand (L = bpy, phen, py) and Control of Semiconducting Properties of ZnS by the Ligand

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If organic ligand can be taken into a semiconducting metal compound like metal sulfide, and if the organic ligand taken into the lattice of the metal compound can control physical properties (*e.g.*, electric conductivity and optical properties) of the metal compound, we may have a new class of industrially-useful semiconductors. However, in spite of many reports on the modification of electric-conducting and optical properties of semiconducting metal chalcogenides by inorganic dopant [1], modification of the physical and chemical properties of the metal chalcogenides by organic ligands [2] has attracted much less attention. As the first step in attempting to control the physical properties of semiconducting metal sulfides by organic ligand, we prepared zinc sulfide containing ligands such as 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), and pyridine (py), and found that the electric conductivity of the ligand-containing ZnS, ZnS·xL, is controlled by the ligand.

When bpy was added to anhydrous ethereal solution of diethylzinc (0.2 M) under an atmosphere of N_2, the solution became red showing instant formation of $Zn(C_2H_5)_2(bpy)$ [3]. Addition of anhydrous H_2S (1.2 mol/mol of diethylzinc) to the red homogeneous solution led to formation of a yellowish-white precipitate and a colorless supernant, with evolution of about 2 mol of C_2H_6 per mol of diethylzinc,

$$Zn(C_2H_5)_2 + n\ bpy + H_2S \longrightarrow \underset{\text{yellowish white}}{ZnS\cdot x(bpy)} + 2C_2H_6 \qquad (1)$$

The yellowish white precipitate was separated by filtration, washed with diethyl ether and hexane repeatedly to remove diethylzinc or bpy, and dried under vacuum to yield an air-stable yellowish solid. Elemental analysis of the solid indicated that the ZnS thus formed contained bpy in its solid structure. Addition of 1,10-phenanthroline (phen) or pyridine (py) instead of bpy in reaction (1) also gave ZnS containing the corresponding ligand in its solid structure. The amount of ligand incorporated into the solid of ZnS varied with the amount of added ligand per mol of diethylzinc, and the result is shown in Fig. 1. It is seen from Fig. 1 that the mol of ligand (L) taken by mol of ZnS (x-value in ZnS·xL) roughly coincides with mol of added ligand per mol of $Zn(C_2H_5)_2$ (n-value = $L/Zn(C_2H_5)_2$) when the amount of the ligand added is small, but it levels off at large n-values. This suggests that bpy can occupy only a limited portion of the lattice points of ZnS. It is known that ZnS adsorbs organic and inorganic compounds on its surface, but the amount of the ligand taken by ZnS in the present study is definitely too large to be explained by adsorption on the surface of ZnS.

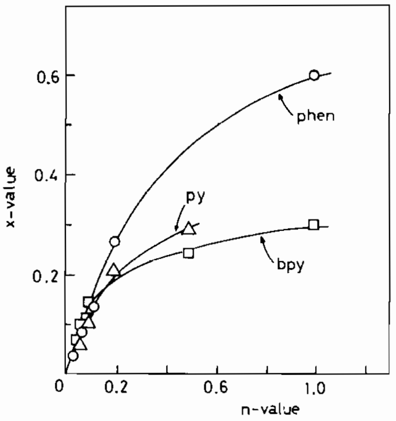

Fig. 1. Amount of ligand taken into the solid of ZnS (x = mol of ligand/mol of ZnS) *vs.* amount of ligand added (n = mol of ligand/mol of $Zn(C_2H_5)_2$).

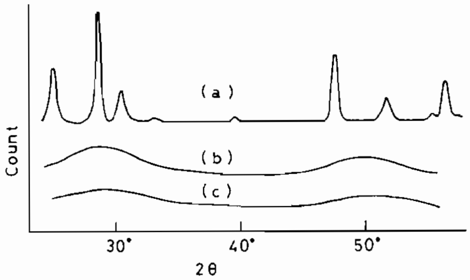

Fig. 2. Powder X-ray diffraction patterns of (a) pure ZnS, (b) ZnS·0.05(bpy), and (c) ZnS·0.34(bpy).

Powder X-ray diffraction patterns of the bpy-containing ZnS becomes very broad on taking bpy into the solid (Fig. 2). The broad diffraction band at 2θ = 28.5° seems to be a overlap of broadened dif-

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fraction bands of ZnS at $2\theta = 26.9°$, $28.5°$ and $30.5°$, whereas another broad diffraction band at about $2\theta = 50°$ is related to diffraction bands of ZnS at $2\theta = 47.5°$, $51.7°$ and $56.3°$. Positions of peaks of the two broad diffraction bands are virtually independent of the x-value of ZnS•x(bpy). These X-ray diffraction data suggest that the lattice structure of ZnS is not extensively destroyed even after incorporation of bpy into ZnS. The phen- and py-containing ZnS showed X-ray diffraction patterns as shown in Fig. 2.

IR spectra of ZnS•xL showed absorption bands characteristic of the ligand. Thermogravimetric analysis of ZnS•xL showed that the ligand usually remained in the solid up to 150 °C. This indicates that the ligand is strongly incorporated in ZnS, supporting a view that most of the ligand does not exist on the surface of ZnS. A reaction of $Zn(C_2H_5)_2$ with H_2S without addition of ligand afforded pure ZnS, as proved by a powder X-ray diffraction pattern of the product. The ligand-containing ZnS could not be obtained by grinding a mixture of ZnS and ligand. Reactions of ZnI_2 with H_2S or Na_2S in the presence of the ligands gave ZnS, but the product did not contain the ligand, as proved by its IR spectrum.

Coloration of ZnS by the incorporation of ligand may be taken as an indication of formation of certain color center due to CT interaction of the ligand with ZnS. However, an UV spectrum of ZnS•xL (in KBr) coincided with a reported UV spectrum of ZnS [4], showing a broad absorption band at about 300 nm. The amount of ligand incorporated into ZnS, on the other hand, strongly influences electric conductivity of the solid, as shown in Fig. 3. The electric conductivity (σ) increases with increase in the x-value at small x-values, reaches a maximum, and decreases with further increase in the x-value*. The observed highest electric conductivity of ZnS•xL was 17, 10^2, and 10^3 times larger, in cases of L = bpy, phen and py respectively, than the electric conductivity ($\sigma = 1.9 \times 10^{-9}$ S cm^{-1}) of undoped ZnS. The increase of σ with increase of x at small x-values may be attributed to formation of a donor level in a band structure of semiconducting ZnS since bpy, phen and py are typical electron donors. The decrease of σ at high x-values may be attributed to morphological change (*e.g.*, change in size of grain) of ZnS or change of mechanism of the electric conduction. The data shown in Fig. 3 have sufficient reproducibility. ZnS•xL catalyzes photochemical evolution of H_2 from a mixture of H_2O and methanol.

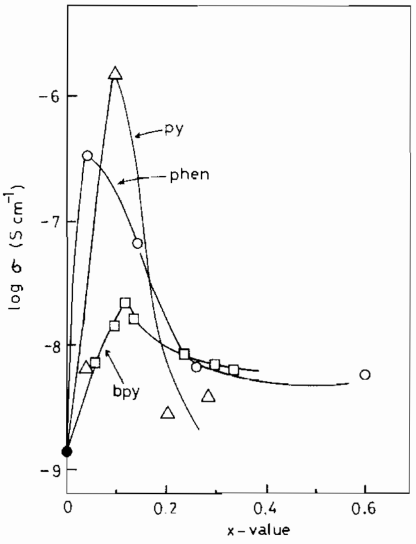

Fig. 3. Dependence of electric conductivity of ZnS•xL on the x-value.

Addition of H_2O instead of H_2S to mixtures of diethylzinc and ligands afforded ZnO•xL. For example, addition of H_2O to a 1:1 adduct of $Zn(C_2H_5)_2$ and bpy gave yellowish-white ZnO•0.036 (bpy), which indicated 50 times larger electric conductivity ($\sigma = 1.6 \times 10^{-5}$ S cm^{-1}) than commercially-available ZnO. Pure ZnO [5] and metal-doped ZnO [6] are now used commercially as sensors of gases; the highly conducting ZnO•0.036(bpy) may be usable as a more effective sensor. The observations described in this paper demonstrate the possibility for preparation of a new class of semiconducting metal chalcogenides which show ligand-controlled electric conductivity and which may find practical uses.

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*The electric conductivity reported in this paper was measured by a four-point method after molding powdery samples into pellets by pressing them at 600 kg/cm^2.

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