

Preparation and Properties of Iron-Doped II-VI Chalcogenides

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Semimagnetic semiconductors are a class of doped II-VI compounds which are of interest in the study of magnetic interactions. Samples of iron-doped ZnS, ZnSe, and CdS were prepared by the direct combination of the elements. Magnetic measurements indicate that the antiferromagnetic interactions of the iron in the zinc systems are greater than those observed in the cadmium chalcogenides. Single crystals of iron-doped zinc chalcogenides were grown by chemical vapor transport. Their IR transmission was measured and the iron concentration for maximum hardness was determined. © 1990 Academic Press, Inc.

Introduction

The substitution of magnetic ions into II-VI semiconductors results in a class of materials known as semimagnetic semiconductors which are of interest to the physics community. The II-VI chalcogenides containing manganese have been extensively studied and their magnetic properties appear to be well understood (1-3). Studies have also been performed where iron is substituted for zinc in the II-VI semiconductors (4-12). The two systems which have received much attention are $Zn_{1-x}Fe_xSe$ and $Cd_{1-x}Fe_xSe$ (8-12). There has, however, been little reported work on the dilute magnetic semiconductors $Zn_{1-x}Fe_xS$ and $Cd_{1-x}Fe_xS$. Barton and Toulmin (13) have reported that the solubility limit of iron in the system $Zn_{1-x}Fe_xS$ was 58 mol% iron. Pappalardo and Dietz (14) studied the spectra of iron-doped CdS; however, no magnetic measurements were performed in their study.

ZnS and ZnSe have been used as IR windows because of their wide transmission range in the infrared. However, both ZnS and ZnSe are soft, which limits their suitability for some applications. It was noted (15, 16) that in the systems $Zn_{1-x}Ni_xS$ and $(GaP)_x(ZnSe)_{1-x}$ the infrared spectra were not changed appreciably from those of pure ZnS and ZnSe, but the hardness was enhanced significantly. Ni(II)($3d^8$) prefers octahedral coordination and it has been shown that it is difficult to introduce a significant quantity of Ni(II) into the tetrahedral structure (15). Since it has been reported that up to 58 mol% iron can be substituted for zinc in $Zn_{1-x}Fe_xS$ at 890°C, it should be possible to modify the properties of II-VI compounds using iron as a component. This paper concerns itself with the preparation and characterization of the systems $Zn_{1-x}Fe_xS(Se)$ for both powder and single crystal samples and $Cd_{1-x}Fe_xS$ for powder samples. The study includes problems associated with attempts to prepare single phase

materials, as well as the magnetic behavior of Fe(II) in a tetrahedral site, IR transmission, hardness, and stability in oxygen.

Experimental

Preparation

Polycrystalline samples were prepared by using stoichiometric amounts of zinc metal (Gallard and Schlesinger, 99.9995%), cadmium metal (Cominco EM 8001, 99.999%), selenium (UMC 23333, 99.999%), iron (Leico 46987) prereduced in Ar/H₂ (85–15), sulfur (Gallard and Schlesinger, 99.999%) sublimed prior to use, and iodine (sublimed, Deepwater Chemical Co., Std. ACS reagent, 99.9%). The appropriate weights of the reactants to give a total weight of 3 g of product were sealed in evacuated 12-mm silica tubes, and heated in the following manner: 500°C for 48 hr, 600°C for 48 hr. The tubes were then transferred to a two-zone furnace and the charge end was maintained at 800°C and the other end at 450°C for 48 hr in order to complete the reaction between the metal and sulfur or selenium without exploding the sample tubes. The samples were then heated at 700°C for 48 hr, 800°C for 48 hr, and 900°C for 96 hr. The samples were intimately mixed after each heat treatment.

Crystal Growth

Stoichiometric amounts of zinc, iron, and sulfur or selenium were placed in a silica tube (14 mm o.d. × 12 mm i.d.) which had been previously heated to near the melting point to minimize any nucleation sites. The tube was evacuated to 10⁻⁵ Torr and freshly sublimed iodine was introduced as the transport agent at a concentration of 5 mg/cc. The tube was sealed off and enclosed in a tightly wound Kanthal coil (to even out temperature gradients) and the whole assembly was placed in a three-zone furnace (17). The crystal growth temperature proce-

dures consisted of setting the furnace to back transport mode for 1 day, equilibrating the furnace to the maximum temperature for 3 hr, and, finally, cooling the growth zone at 1°C/hr to the growth temperature. Optimum crystal growth for Zn_{1-x}Fe_xS and Zn_{1-x}Fe_xSe occurred when the charge zone was maintained at 965°C and the growth zone at 870°C. The transport process was carried out for 5 days and the typical crystal size was 3 × 3 × 1 mm. The actual composition of the single crystal was determined from the magnetic measurements.

Characterization of Products

X-ray powder diffraction patterns of the samples were obtained using a Philips diffractometer and monochromated high intensity CuKα₁ radiation (λ = 1.5405 Å). For qualitative phase identification, diffraction patterns were taken over the range 12° < 2θ < 72° with a scan rate of 1° 2θ/min, while cell parameters were determined from scans taken with a scan rate of 0.25° 2θ/min. Precise lattice parameters were obtained from the diffraction peaks using a least-squares refinement program which corrects for the systematic errors of the diffractometer.

Optical measurements on polished single crystals were performed at room temperature with a Perkin-Elmer 580 single beam scanning infrared spectrophotometer. The measurements were performed in the transmission mode over the range 2.5–25 μm. Transmission through the sample was normalized to the signal obtained in the absence of the sample.

Microhardness measurements (Knoop indenter) were made on crystals using a Krypton microhardness tester. The results were obtained using a diamond indenter with loads of 25 g for Zn_{1-x}Fe_xS and 10 for Zn_{1-x}Fe_xSe.

The stability of these compounds toward oxidation was determined by heating them in a flowing oxygen stream (60 scfm) and monitoring the change in weight during the

heating period. The decomposition temperature was determined as the temperature where the weight of the sample began to change.

Magnetic susceptibilities were measured from liquid nitrogen temperature (77 K) to 500 K using a Faraday balance at a field strength of 10.4 kOe. Honda-Owens (field dependency) plots were also made and all magnetic susceptibility data were corrected for diamagnetism.

Results and Discussion

Polycrystalline samples of $Zn_{1-x}Fe_xS$, $Zn_{1-x}Fe_xSe$, and $Cd_{1-x}Fe_xS$ were prepared directly from the elements. Samples of $Cd_{1-x}Fe_xSe$ have been prepared and studied by Smith *et al.* (12). X-ray diffraction patterns indicated that the zinc iron sulfide and zinc iron selenide products were single phase and crystallized with the cubic zinc blende structure. The cadmium iron sulfide and cadmium iron selenide also were single phase and crystallized with the hexagonal wurtzite structure.

For the system $Zn_{1-x}Fe_xS$, compositions were chosen where $x = 0.03, 0.10, 0.15, 0.25, \text{ and } 0.30$. It was found for this system that the limit of solubility of iron in ZnS was 30 at.% for the above method of preparation. It was also found that the 30% sample appeared to be single phase by X-ray diffraction; however, the magnetic susceptibility showed field-dependent behavior (Fig. 1), indicating the presence of an impurity with a spontaneous moment; this magnetic impurity decreased with continued heating. Although the sample where $x = 0.30$ appeared single phase by X-ray diffraction after only 4 days of reaction time at 900°C, it was found that 16 additional days of heating at 900°C were necessary in order to obtain a field-independent material (Fig. 1). This result demonstrated the importance of magnetic susceptibility measurements in determining completeness of reaction in the system

$Zn_{1-x}Fe_xS$. The maximum solubility limit of iron in zinc sulfide has previously been determined by Barton and Toulmin (13) to be 58 mol% iron at 890°C. The samples in their studies took an average of 6 months to show single phase material as indicated by X-ray diffraction analysis. Furthermore, it was found that control of the sulfur pressure was necessary for the preparation of samples containing high iron content.

For the system $Zn_{1-x}Fe_xSe$, compositions were chosen where $x = 0.03, 0.10, 0.15, 0.20, \text{ and } 0.25$. All samples appeared to be single phase as indicated by X-ray diffraction analysis; however, the $x = 0.25$ sample showed field-dependent behavior. Unlike the $Zn_{.70}Fe_{.30}S$ sample, continued heating of the selenide did not improve its field-dependent behavior. Therefore, the solubility limit of iron in zinc selenide is between 20 and 25 at.% iron. This limit of solubility of iron in zinc selenide is in agreement with the work of Twardowski, who reported that a maximum of 22 mol% iron could be substituted for zinc in ZnSe boules grown from the melt (8).

For the system $Cd_{1-x}Fe_xS$, compositions were chosen where $x = 0.03, 0.10, 0.15, 0.20, \text{ and } 0.25$. All samples appeared to be single phase as indicated by X-ray diffraction analysis. The $x = 0.25$ sample showed field-dependent behavior, but became field independent after 12 additional days of heating at 850°C. Thus, 25 at.% appears to be the solubility limit of Fe in CdS.

For all the samples listed in Table I, the magnetic moment per Fe(II) obtained from magnetic susceptibility data remains 5.4(1) μ_B regardless of iron content. The Weiss constants are negative, indicating antiferromagnetic Fe-Fe interactions, and become more negative with increasing iron substitution for zinc or cadmium. The Weiss constants of the $Zn_{1-x}Fe_xS$ and $Zn_{1-x}Fe_xSe$ systems are essentially the same. The Weiss constants of the $Cd_{1-x}Fe_xS$ and $Cd_{1-x}Fe_xSe$ systems are also equivalent, but are mark-

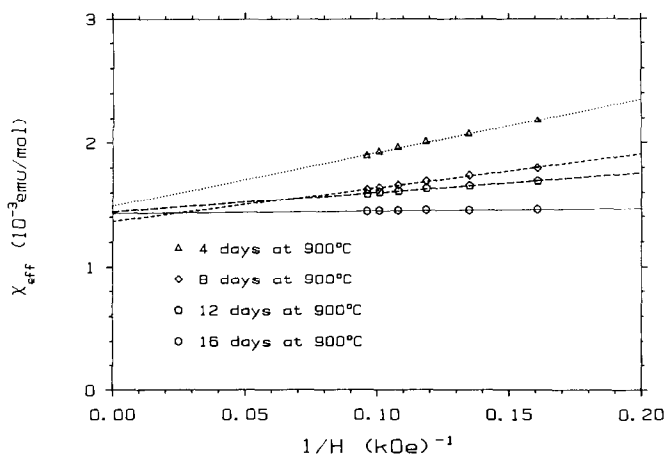


FIG. 1. $\text{Zn}_{70}\text{Fe}_{30}\text{S}$. Variation of effective magnetic susceptibility with inverse magnetic field as a function of time-at-temperature.

edly smaller than those obtained for the zinc systems, which indicates that weaker anti-ferromagnetic interactions occur in the cadmium systems. This difference in the strength in antiferromagnetic interactions

has been also observed when cobalt is substituted for zinc and cadmium in these systems. Niu *et al.* (18) indicated that the observed differences in the strength of the antiferromagnetic interactions were related to the increase in the Co-Co effective distances in the cadmium systems.

TABLE I
SUMMARY OF PROPERTIES OF IRON-SUBSTITUTED
II-VI CHALCOGENIDES

Compound	Cell constant (Å)		Moment (μ_B)	Weiss constant (K)	Cell volume (Å ³)
	<i>a</i>	<i>c</i>			
ZnS	5.409(2)	—	—	—	—
Zn ₉₇ Fe ₀₃ S	5.410(2)	—	5.3	-55(5)	—
Zn ₉₀ Fe ₁₀ S	5.415(2)	—	5.5	-184(5)	—
Zn ₈₅ Fe ₁₅ S	5.417(2)	—	5.4	-224(5)	—
Zn ₇₅ Fe ₂₅ S	5.418(2)	—	5.4	-365(5)	—
Zn ₇₀ Fe ₃₀ S	5.420(2)	—	5.5	-564(5)	—
ZnSe	5.667(2)	—	—	—	—
Zn ₉₇ Fe ₀₃ Se	5.668(2)	—	5.2	-49(5)	—
Zn ₉₀ Fe ₁₀ Se	5.675(2)	—	5.5	-166(5)	—
Zn ₈₅ Fe ₁₅ Se	5.676(2)	—	5.3	-199(5)	—
Zn ₈₀ Fe ₂₀ Se	5.677(2)	—	5.4	-284(5)	—
CdS	4.136(2)	6.715(2)	—	—	—
Cd ₉₇ Fe ₀₃ S	4.126(2)	6.700(2)	5.3	-23(5)	—
Cd ₉₀ Fe ₁₀ S	4.105(2)	6.667(2)	5.3	-85(5)	—
Cd ₈₅ Fe ₁₅ S	4.094(2)	6.651(2)	5.4	-135(5)	—
Cd ₈₀ Fe ₂₀ S	4.079(2)	6.634(2)	5.3	-149(5)	—
CdSe ^a	—	—	—	—	112.3
Cd ₉₈ Fe ₀₂ Se ^a	—	—	5.3	-17	112.0
Cd ₉₅ Fe ₀₅ Se ^a	—	—	5.6	-41	111.6

^a Obtained from Smith *et al.* (12); cell volume is expressed instead of cell constants.

Single crystals of $\text{Zn}_{1-x}\text{Fe}_x\text{S}$ and $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$ were grown by chemical vapor transport using iodine as the transport agent. All of the products crystallized with the cubic zinc blende structure and showed field-independent behavior. The iron concentration of crystals was obtained by comparing their room temperature susceptibilities with the susceptibilities obtained from polycrystalline samples of known iron content (Fig. 2). Several crystals of each system were grown and their IR properties as well as their hardness and thermal stability were determined (Table II). It can be seen that the addition of iron below 16 mol% did not affect transmission at the long wavelength end, but a cutoff was observed at the high energy end.

Hardness measurements were made on these samples and showed that initially the addition of iron caused an increase in hardness. Larger substitutions of iron did not

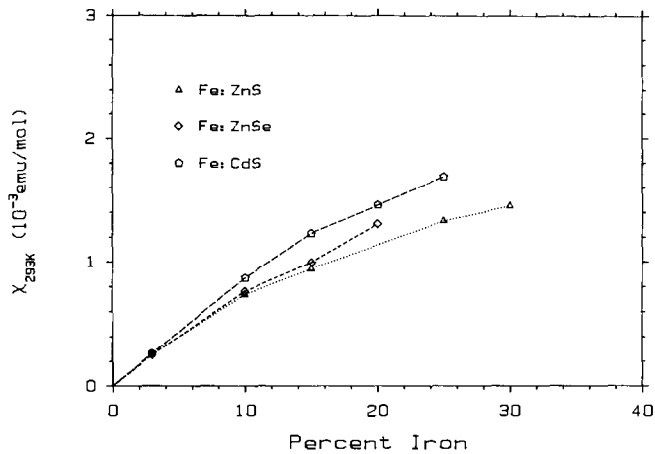


FIG. 2. Polycrystalline standards. Variation of magnetic susceptibility with composition of standard polycrystalline samples of ZnS, ZnSe, and CdS.

TABLE II
PROPERTIES OF SINGLE CRYSTALS OF $Zn_{1-x}Fe_xS$ AND $Zn_{1-x}Fe_xSe$

x	Hardness (kg/mm ²)	IR transmission (μm)	Thermal stability ($^{\circ}C$)
		$Zn_{1-x}Fe_xS$	
0.00	158	2.5–14	520
0.03	176	6.0–14	530
0.10	184	6.0–14	540
0.16	180	6.0–12	540
		$Zn_{1-x}Fe_xSe$	
0.00	104	2.5–20	420
0.03	149	6.0–20	380
0.10	136	6.5–20	360
0.16	136	6.5–18	370

further affect the hardness. Thermal stability measurements showed that there was very little affect on the thermal stability as the amount of iron substituted for zinc was increased in these systems.

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References

1. N. B. BRANDT AND V. V. MOSHCHALOV, *Adv. Phys.* **33**, 193 (1984).
2. J. K. FURDYNA, *J. Appl. Phys.* **53**, 7637 (1982).
3. J. K. FURDYNA AND N. SMARATH, *J. Appl. Phys.* **61**, 3526 (1987).
4. A. K. KOMAROV, S. M. RYABCHENKO, AND O. V. TERLETSKI, *Phys. Status Solidi B* **102**, 603 (1980).
5. W. LAW AND M. WEGER, *Phys. Rev.* **118**(5), 1130 (1960).
6. A. PETROU, X. LIU, G. WAYTENA, J. WARNOCK, AND W. GIRIAT, *Solid State Commun.* **61**, 767 (1987).
7. D. HEIMAN, A. PETROU, E. D. ISAACS, S. H. BLOOM, Y. SHAPIRA, AND W. GIRIAT, *Phys. Rev. Lett.* **60**, 1876 (1988).
8. A. TWARDOWSKI, P. GOLD, W. J. M. DE JONGE, AND M. DEMEANIUK, *Solid State Commun.* **64**, 63 (1987).
9. H. SWAGTEN, A. TWARDOWSKI, AND W. J. M. DE JONGE, *Phys. Rev. B* **39**(4), 2568 (1989).
10. A. TWARDOWSKI, A. LEWICKI, M. ARCISZEWSKA, W. J. M. DE JONGE, H. SWAGTEN, AND M. DEMEANIUK, *Phys. Rev. B* **38**(15), 10–749 (1988).
11. A. TWARDOWSKI, M. VON ORTENBERG, AND M. DEMEANIUK, *J. Cryst. Growth* **72**, 401 (1985).
12. K. SMITH, J. MARSELLA, K. DWIGHT, AND A. WOLD, *Mater. Res. Bull.* **23**, 1423 (1988).

13. P. BARTON AND P. TOULMIN, *Econ. Geol.* **61**(5), 815 (1966).
14. R. PAPPALARDO AND R. DIETZ, *Phys Rev.* **123**(4), 1188 (1961).
15. P. W. R. KERSHAW, K. DWIGHT, AND A. WOLD, *Mater. Res. Bull.* **24**, 49 (1989).
16. H-S. SHEN, G-Q. YAO, X-C. HE, K. DWIGHT, AND A. WOLD, *Mater. Res. Bull.* **23**, 153 (1988).
17. R. KERSHAW, M. VLASSE, AND A. WOLD, *Inorg. Chem.* **6**, 1599 (1967).
18. C-M. NIU, R. KERSHAW, K. DWIGHT, AND A. WOLD, *J. Solid State Chem.*, submitted for publication.