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by

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Preparation of compounds with the tetrahedral structure which transmit in the far infrared

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ABSTRACT

A number of chalcogenides and phosphides crystallize with the tetrahedral structure in which the cations and anions are in tetrahedral positions. The II-VI compounds such as ZnS, ZnSe, CdS and CdSe are known to transmit in the far infrared. However, they are soft and decompose in air at relatively low temperatures. Efforts have been made at Brown University to improve the properties of these compounds, either by alloying them with III-V semiconductors, or by substituting transition metals such as nickel for the divalent specie.

1. INTRODUCTION

The development of new synthetic techniques is necessary if the search for mechanically sound, hard transparent far infrared materials is to be successful. Such compounds will probably be broad band semiconductors which are either sulfoselenides, phosphides or phosphochalcogenides.

High temperature synthesis will be limited by loss of the anion species and hence low temperature methods must be utilized if successful synthesis is to be achieved. Recent studies [1,2] have been carried out at Brown University in which single crystals of $ZnSiP_2$, $ZnGeP_2$, $ZnGeP_{1.8}As_{.2}$ and $ZnGeP_{1.6}As_{.4}$ have been grown by several techniques and their electronic and optical properties were compared. Further study has resulted in the preparation of a group of quaternary chalcogenides crystallizing with the Wurtz-stannite structure[3]. These compounds were prepared by chemical vapor transport and characterized. Several of the phosphides and chalcogenides transmitted beyond 12 microns, and $ZnGeP_2$ was stable in air up to 740°C and Cu_2ZnGeS_4 was stable up to 620°C. Both compounds were found to have considerable hardness as well as stability.

In a recent study[4], the work was extended to an examination of $(ZnSe)_{1-x}(GaP)_x$ solid solutions. It was found that the IR spectrum of $(ZnSe)_{0.905}(GaP)_{.095}$ was not appreciably changed from that of pure ZnSe; however, the hardness and stability towards oxidation were greatly enhanced.

In addition to a program which is directed towards the search for new IR materials, an effort is also being made to improve the mechanical properties and stability of both ZnS and ZnSe.

ZnS is used as an IR window material because of its wide transmission range in the infrared. However, ZnS is soft, which limits its suitability for some applications. It was anticipated that the hardness of ZnS might be improved by the introduction of transition metals, such as nickel, into its structure.

Little work has been reported on the system $Ni_xZn_{1-x}S$, because Ni(II)($3d^8$) prefers octahedral sites and is therefore difficult to introduce into the tetrahedral ZnS structure. Czamanske and Goff[5] reported that the solubility of NiS in ZnS at 755°C was only 1.16 mole percent. Some recent spectroscopic studies[6,7] have been carried out on zinc sulfide samples doped with Ni(II). However, there has been no report on the IR transmission, magnetic properties, hardness and stability of nickel doped zinc sulfide crystals. It is the purpose of this study to investigate the properties of such materials and compare the results with those obtained for pure ZnS.

2. EXPERIMENTAL

2.1 Single crystal growth

Single crystals of ZnS and $Ni_xZn_{1-x}S$, where x = 0.03, have been grown by chemical vapor transport using iodine as the transport agent. The zinc metal (Gallard and Schlesinger 99.9995%) was prereduced in an Ar/H_2 (85/15) atmosphere at 200°C for 3 hours. Sulfur (Gallard and Schlesinger 99.999%) was sublimed prior to use.

For ZnS crystals, stoichiometric weights of zinc and sulfur were introduced into silica tubes which were then evacuated to 10^{-5} torr, and 5mg/cc of iodine were added. The tubes were 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. The crystal growth temperature program consisted of setting the furnace to back transport mode for one day (growth zone at 1000°C and charge zone at 800°C), equilibrating the furnace to the maximum reaction temperature for three hours, and finally, cooling the central zone at 1°C/hr to the growth temperature. Optimum crystal growth occurred when the charge zone was maintained at 950°C and the growth zone at 925°C. The transport process was carried out for a week, and the typical crystal size was 5x3x3 mm. For the growth of nickel doped ZnS crystals, stoichiometric weights of metals and sulfur with various nickel to zinc ratios were introduced into a silica tube and evacuated. The growth of crystals was achieved by the above-described transport process. The real compositions of the crystals grown were determined by magnetic measurements.

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2.2 Characterization

X-ray powder diffraction patterns of ground single crystals were obtained using a Philips diffractometer and monochromated high intensity $CuK\alpha_1$ radiation (λ = 1.5405A). For qualitative phase identification, diffraction patterns were taken over the range 12° < 2θ < 80° with a scan rate of 1° 2θ/min, while cell parameters were determined from scans taken at 0.25° 2θ/min. Precise lattice parameters were obtained from these reflections using a least-squares refinement program which corrects for the systematic errors of the diffractometer.

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

The microhardness measurements (Knoop indenter) were made on crystals using a Kentron microhardness tester. The results were obtained using a diamond indenter with 25 gram loads.

The stability of these compounds toward oxidation was determined by heating them in a flowing oxygen stream (60cc/min) 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. The results are summarized in Table 1.

Magnetic susceptibilities were measured from liquid nitrogen temperature to 315 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[8].

TABLE 1. Properties of $Ni_xZn_{1-x}S$

x	Phase	Cell Parameter	IR Transmission Range (μm)	Knoop Hardness	Decomposition Temperature (°C)
0	Cub.ZnS	a = 5.411(2)	2.5 - 14	158 ± 9	520
0.03	Cub.ZnS	a = 5.409(2)	3.5 - 14	251 ± 36	490

3. RESULTS AND DISCUSSION

Single crystals of ZnS and $Ni_{0.03}Zn_{0.97}S$ have been grown by chemical vapor transport using iodine as the transport agent. The crystals averaged 5x3x3 mm in size. Pure zinc sulfide was colorless and nickel-doped zinc sulfide was dark red in color. The exact concentration of nickel in the crystals was determined by magnetic measurements The properties of these compounds are summarized in Table 1.

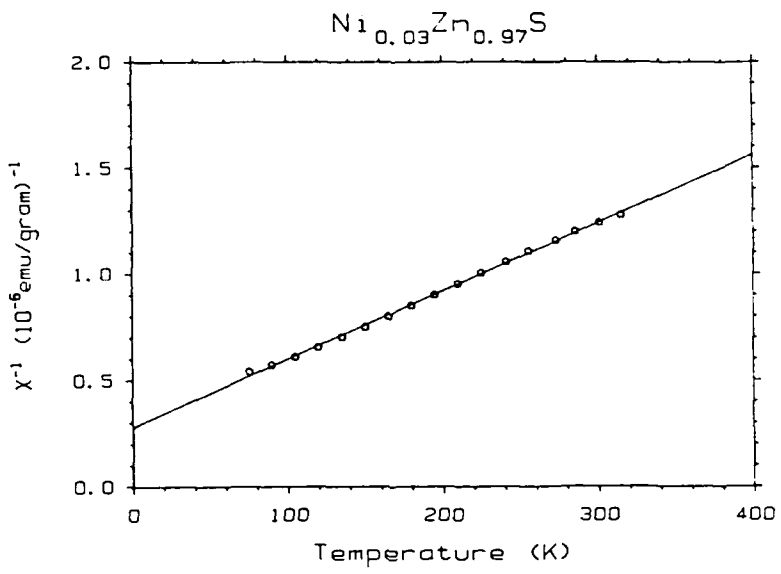

Fig. 1. Variation of magnetic susceptibility with temperature for a typical crystal of $Ni_xZn_{1-x}S$. The composition $Ni_{0.03}Zn_{0.97}S$ was calculated from the slope of the fitted line assuming the spin-only moment of 2.83 BM per Ni(II).

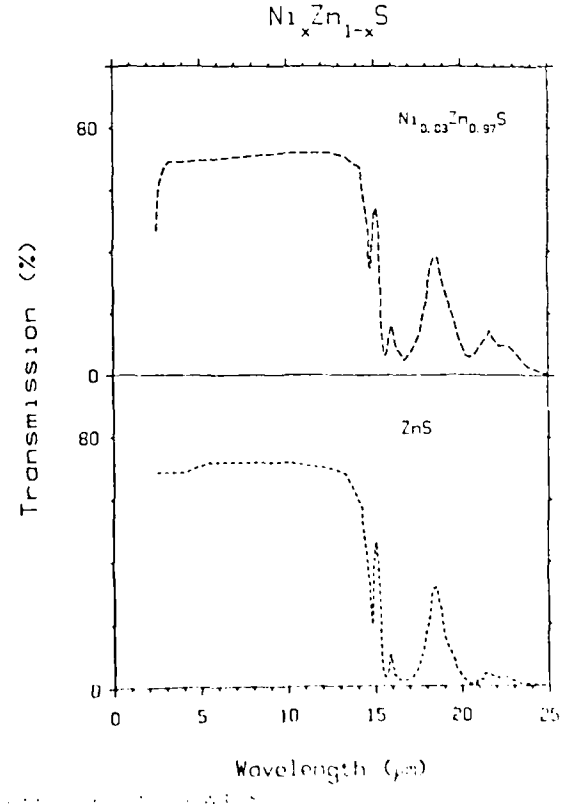

Fig. 2. The infrared spectrum of a crystal of $Ni_{0.03}Zn_{0.97}S$ compared with that of pure ZnS.

Magnetic measurements were made as functions of both field and temperature. All samples, doped with nickel, showed identical paramagnetic behavior and had no field dependency at either room temperature or at liquid nitrogen temperature. The reciprocal magnetic susceptibility is plotted versus temperature in Fig. 1 and shows Curie-Weiss behavior with a Weiss constant of -78 K. The concentration of nickel can be calculated from the slope of the experimental line, by assuming a spin-only moment (2.83 B.M.) for Ni(II). It was found that crystals grown from the charge containing nickel to zinc ratios of either 10/90 or 15/85 gave identical nickel contents of 3 atomic percent. This indicated that the maximum solubility at the growth conditions had been reached.

The crystalline structures of these compounds were determined by x-ray powder diffraction analysis. Both pure ZnS crystals and ZnS crystals containing 3% nickel have the cubic stannite structure. Cell parameters obtained from a least-squares refinement showed that there was no significant change in cell parameter when 3% nickel was substituted into zinc sulfide.

The IR transmission data summarized in Table 1 are plotted in Fig. 2. The results indicate that pure ZnS crystals transmit in the range of 2.5 μm to 14 μm. The crystals containing 3 atomic percent nickel gave the same IR transmission at the long wavelength end, but there appeared to be a cut off at 3.5 μm.

Hardness (Knoop hardness number) of these compounds and their thermal stability towards oxidation are also given in Table 1. The hardness of pure zinc sulfide is 158, which is in agreement with the previous work[9], where a value of 185 was measured with a Vickers indenter. The samples doped with only 3% nickel are significantly harder than pure zinc sulfide and gave a Knoop hardness number of 251. Pure ZnS begins to decompose in flowing oxygen at 520°C and the samples containing 3 atomic percent nickel begin to decompose at 490°C.

4. CONCLUSIONS

It was found that, whereas ZnS doped with 3% nickel has a cut off at the short wavelength end of its IR spectrum, it provides the same IR transmission as pure ZnS at the long wavelength end. The hardness of ZnS is significantly increased by nickel doping. This should be helpful for its use as an IR window material in the range of 8 to 12 μm. Furthermore, this type of substitution can also be made of ZnSe and the system $Zn_{1-x}Ni_xSe$ is presently under investigation.

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