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The Crystal Growth and Characterization of the Solid Solutions $(ZnS)_{1-x}(CuGaS_2)_x$

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Single crystals of members of the system $(ZnS)_{1-x}(CuGaS_2)_x$ (x = 0, 0.053, 0.103, 1.00) were grown by chemical vapor transport using iodine as the transport agent. The IR transmission range of $(ZnS)_{0.947}(CuGaS_2)_{0.053}$ and $(ZnS)_{0.897}(CuGaS_2)_{0.103}$ is narrower than that observed for pure ZnS. However, these materials still show good transmission in the long wavelength IR range. The addition of small amounts of $CuGaS_2$ increased the hardness and thermal stability of ZnS. Therefore, these materials may be useful for the development of IR windows in the long wavelength range.

Introduction

ZnS crystallizes with the cubic zinc blende structure (Fig. 1) (space group $F\bar{4}3m$) below 1020°C and the hexagonal wurtzite structure (space group $C6mc$) above the phase transition temperature. ZnS has been studied extensively because it offers a variety of unique device applications. It can be used as a good IR window material because of its wide transmission range in the far infrared. However, ZnS is relatively soft, which limits its suitability for some applications (*1*). The ternary sulfide, $CuGaS_2$, crystallizes with the chalcopyrite structure (Fig. 2) (space group $I\bar{4}2d$), which is closely related to the zinc blende structure. In the chalcopyrite structure, there is an ordering of Cu(I) and Ga(III) ions on the cation sites of zinc blende which results in a doubling of the c-axis. X-C. He *et al.* (*2*) reported that $CuGaS_2$ transmitted in the far infrared range and was also considerably harder, but more brittle, than ZnS. It was noted (*1, 3–5*) that the various compounds in the systems $Zn_{1-x}Ni_xS$, $(GaP)_x(ZnSe)_{1-x}$, $Zn_{1-x}Fe_xS$, and $Zn_{1-x}Co_xS$ gave infrared spectra similar to those of pure ZnS and ZnSe if the value of $x < 0.1$. In addition, the hardness of these materials was increased significantly. Therefore, it was decided to study the crystal growth and characterization of $(ZnS)_{1-x}(CuGaS_2)_x$ systems in order to observe any increased hardness of ZnS and to determine if these materials could have useful optical or mechanical properties.

There have been relatively few studies carried out on the preparation and characterization of solid solutions formed between ZnS and $CuGaS_2$. Apple (*6*) and Robbins and Miksovsky (*7*) have reported the extent of solid solutions $(ZnS)_{1-x}(CuGaS_2)_x$ and determined their optical properties. Because of similarities in structure, unit cell dimensions, and bond type, $CuGaS_2$ is to-

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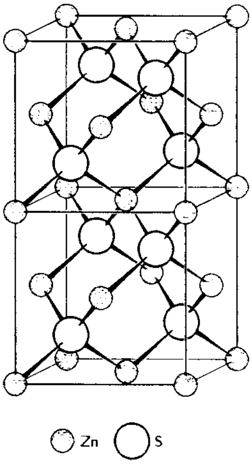

FIG. 1. Crystal structure of ZnS (cubic zinc blende).

tally miscible with ZnS. In the ZnS–$CuGaS_2$ system, the zinc blende structure is formed for up to 40 mole% $CuGaS_2$, and the chalcopyrite structure is formed from 50 to 100 mole% $CuGaS_2$. Members of the solid solution between ZnS and $CuGaS_2$ with the zinc blende structure should be studied to determine if they transmit in the far infrared range and if they are harder than pure ZnS.

Single crystals of ZnS (*1*, *8*, *9*) and Cu GaS_2 (*2*, *10*, *11*), suitable for characterization, have been grown by chemical vapor transport using iodine as the transport agent. This method has been shown to produce crystals at a lower temperature than can be obtained from the melt. In addition, Donohue and Bierstedt (*12*) have shown that single crystals of solid solutions formed between ZnS and $CuAlS_2$ can be obtained using the chemical vapor transport technique. Therefore, this method is used in this study to prepare crystals of $(ZnS)_{1-x}(CuGaS_2)_x$. Polycrystalline samples can also be prepared by the direct combination of zinc, copper, gallium, and sulfur elements. The synthesis of these crystals has made it possible to determine their IR transmission, thermal stability, and hardness relative to pure ZnS.

Experimental

Preparation of Polycrystalline Samples

Members of the system $(ZnS)_{1-x}$ $(CuGaS_2)_x$ were prepared by the following procedure: polycrystalline samples with different compositions were prepared by using stoichiometric amounts of zinc (Gallard and Schlesinger 99.9995%) sublimed prior to use, copper (Johnson Matthey 99.999%) prereduced in Ar/H_2 (85/15), gallium (Johnson Matthey 99.999%) and sulfur (Gallard and Schlesinger 99.999%) sublimed prior to use. Appropriate weights of the reactants to give a total weight of 2 g of product were sealed in evacuated cylindrical 12-mm i.d. × 60-mm silica tubes. In order to complete the reaction between the metal and sulfur without exploding the sample tubes, the tubes were heated to 400, 500, 600, and 700°C and held for 24 hr at each temperature. They were then heated up to 800°C and held at that temperature for 72 hr. The samples were then

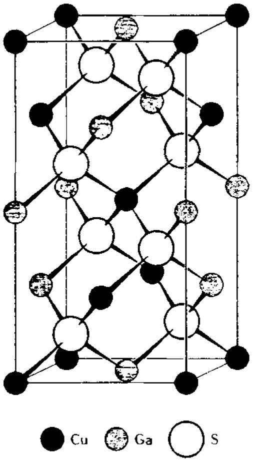

FIG. 2. Crystal structure of $CuGaS_2$ (tetragonal chalcopyrite).

ground under a nitrogen atmosphere and reheated for 24 hr at 800°C. The samples were intimately mixed after each heat treatment. Finally, the samples were cooled in the furnace to room temperature before removal.

Crystal Growth

Single crystals of ZnS, $CuGaS_2$, and $(ZnS)_{1-x}(CuGaS_2)_x$ were grown by chemical vapor transport using iodine as the transport agent. The reactants were introduced into a silica tube (14-mm o.d., 12-mm i.d. × 300-mm) which had been previously heated to near its melting point in order to minimize any nucleation sites. The tube was evacuated to 10^{-5} Torr, and freshly sublimed iodine (Deepwater Chemical Co., Std. ACS reagent 99.9%) was introduced as the transport agent at a concentration of 5 mg/ml. 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. The crystal growth temperature program consisted of setting the furnace to back transport mode for 1 day, equilibrating the furnace to the charge temperature for 3 hr, and, finally, cooling the growth zone at 1°C/hr to the growth temperature (*13*). Optimum crystal growth for ZnS occurred when the charge zone was maintained at 950°C and the growth zone at 925°C, and that for $(ZnS)_{1-x}(CuGaS_2)_x$ ($x = 0.05$ and 0.10) occurred when the charge zone was kept at 850°C and the growth zone at 810°C (Table I). The optimum crystal growth for $CuGaS_2$ took place when the charge zone was maintained at 1000°C and the growth zone at 950°C. The transport process was carried out for 1 week for ZnS and $(ZnS)_{1-x}(CuGaS_2)_x$, and for 2 weeks for $CuGaS_2$. The typical crystal sizes of different compositional crystals are also given in Table I. The actual compositions of the crystals grown were determined from comparison of their cell parameters with those obtained from polycrystalline samples of known stoichiometry.

TABLE I

GROWTH CONDITIONS FOR SINGLE CRYSTALS AND CRYSTAL SIZE

Compound	Charge temperature (°C)	Growth temperature (°C)	Crystal size (mm)
ZnS	950	925	10 × 6 × 2
$(ZnS)_{0.95}(CuGaS_2)_{0.05}$[a]	850	810	6 × 3 × 2
$(ZnS)_{0.90}(CuGaS_2)_{0.10}$[a]	850	810	10 × 8 × 3
$CuGaS_2$	1000	950	9 × 3 × 2

[a] Nominal composition.

Characterization of Products

X-ray powder diffraction patterns of the samples were obtained using a Philips diffractometer and monochromated high intensity $CuK\alpha_1$ radiation ($\lambda = 1.5405$ Å). For qualitative phase identification, diffraction patterns were taken over the range $12° < 2\theta < 80°$ 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 the diffraction peaks using a least-squares refinement program which corrects for the systematic errors of the diffractometer.

Selected single crystals were polished on opposite faces with progressive suspensions of 1, 0.3, and 0.05 μm alumina on alpha A polishing cloth (Mark V Laboratory) using a Minimet polisher. Optical measurements were performed at room temperature on a Perkin–Elmer 580 double scanning infrared spectrophotometer. The measurements were carried out in the transmission mode over the range 2.5–50 μm. Transmission through the sample was normalized to the signal obtained in the absence of the sample.

Microhardness measurements (Knoop indenter) were made on polished single crystal using a Kentron microhardness tester. The results were obtained using a diamond indenter with a 25-g load for ZnS and $(ZnS)_{1-x}(CuGaS_2)_x$, and a 10-g load for $CuGaS_2$.

The stability of these compounds toward oxidation was determined by grinding a small crystal and heating the resulting powder in flowing oxygen (60 ml/min) and monitoring the change in weight during the heating period. The decomposition temperature was determined as the temperature where the weight of sample began to change.

Results and Discussion

Polycrystalline samples of $(ZnS)_{1-x}(CuGaS_2)_x$ were prepared directly from the elements. X-ray diffraction patterns indicated that $(ZnS)_{1-x}(CuGaS_2)_x$ polycrystalline samples were single phase and crystallized with the cubic zinc blende structure for up to 30 mole% $CuGaS_2$. The pure ZnS polycrystalline sample was colorless, and the solid solutions formed between ZnS and $CuGaS_2$ changed in color from yellow to dark yellow according to the increased content of $CuGaS_2$. Samples with different amounts of $CuGaS_2$ were subjected to X-ray analysis in order to obtain their cell parameters. The cell parameters are plotted as a function of $CuGaS_2$ concentration for $(ZnS)_{1-x}(CuGaS_2)_x$ in Fig. 3. At $CuGaS_2$ concentrations less than 30.0 mole%, the cell parameters decrease linearly with increasing amounts of $CuGaS_2$. This is in good agreement with the results reported by Apple (*6*). This linear relationship between cell parameters and concentration of $CuGaS_2$ can be used to calculate the composition of unanalyzed single crystals.

Single crystals of $(ZnS)_{1-x}(CuGaS_2)_x$ were grown by chemical vapor transport using iodine as the transport agent. The compositions of the crystals were determined by comparing their cell parameters with those obtained from a plot of cell parameter vs composition for the standard polycrystalline materials. The results of these determinations are given in Table II. It can be seen that the transported crystals contain almost the identical concentration of $CuGaS_2$ as the original charge. The hardness, as determined by the Knoop method, is also given in Table II for these single crystals. As previously reported (*1*), $CuGaS_2$ is much harder than ZnS. The hardness of pure ZnS is 153 Kg/mm², which is in agreement with previous investigations (*2–5*); the hardness of $(ZnS)_{0.947}(CuGaS_2)_{0.053}$ and $(ZnS)_{0.897}(CuGaS_2)_{0.103}$ are 250 Kg/mm² and 298 Kg/mm², respectively. Therefore, the introduction of $CuGaS_2$ into ZnS increases its hardness. The thermal stability, in a flowing oxygen atmosphere, of $CuGaS_2$ is higher than that of ZnS (Table II). Solid solutions in which 5.3 and 10.3 mole% of ZnS are replaced by $CuGaS_2$ begin to decompose at temperatures higher than both end members. Thus it can be seen that the introduc-

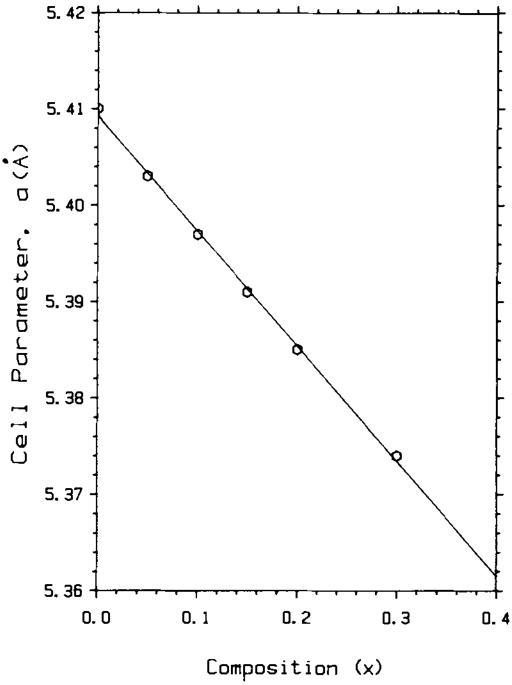

FIG. 3. Variation of cell parameter with $CuGaS_2$ concentration in $(ZnS)_{1-x}(CuGaS_2)_x$.

TABLE II

PROPERTIES OF $(ZnS)_{1-x}(CuGaS_2)_x$ SINGLE CRYSTALS

Nominal comp. (x)	Crystal comp. (x)	Cell dim. (Å)	Knoop hardness (Kg/mm^2)	Decomposition temperature (°C)	Infrared transmission (μm)
0.0	0.0	5.410(2)	153(10)	570	2.5–14
0.05	0.053	5.403(2)	250(10)	670	4.5–13
0.10	0.103	5.397(2)	298(20)	680	4.5–13
1.0	1.0	5.362(2) 10.495(2)	387(40)	628	4.5–13

tion of $CuGaS_2$ into ZnS increases its stability toward oxidation.

The IR transmission data summarized in Table II are plotted in Fig. 4. The results indicate that pure ZnS transmits in the range of 2.5 to 14.0 μm and pure $CuGaS_2$ crystals transmit in the range of 4.5 to 13.0 μm. These values are in good agreement with previous reports (*1*–*5*). Crystals of the solid solutions formed between ZnS and $CuGaS_2$ transmit in the range of 4.5 to 13.0 μm. Even though the IR transmission range for $(ZnS)_{0.947}(CuGaS_2)_{0.053}$ and $(ZnS)_{0.897}(CuGaS_2)_{0.103}$ is narrower than that for pure ZnS, these materials still show good IR transmission at 10 μm. Furthermore, their hardness values and thermal stability are substantially better than those of pure ZnS. Therefore, the solid solutions formed between ZnS and $CuGaS_2$, having the zinc blende structure, are potentially good candidates for IR window materials.

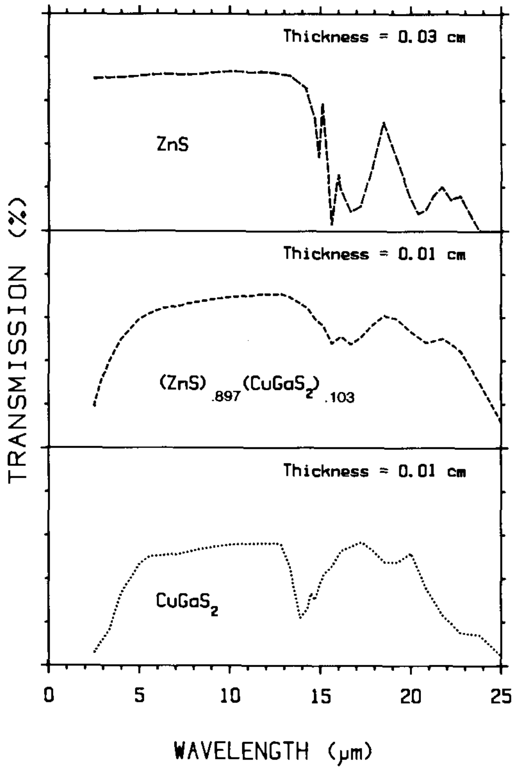

FIG. 4. Infrared transmission (0–100%) of ZnS, $(ZnS)_{0.897}(CuGaS_2)_{0.103}$, and $CuGaS_2$.

Acknowledgments

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References

1. P. WU, R. KERSHAW, K. DWIGHT, AND A. WOLD, *Mater. Res. Bull.* **24**, 49 (1989).
2. X-C. HE, H-S. SHEN, P. WU, K. DWIGHT, AND A. WOLD, *Mater. Res. Bull.* **23**, 799 (1988).
3. H-S. SHEN, G-Q. YAO, X-C. HE, K. DWIGHT, AND A. WOLD, *Mater. Res. Bull.* **23**, 153 (1988).
4. J. DICARLO, M. ALBERT, K. DWIGHT, AND A. WOLD, *J. Solid State Chem.* **87**, 443 (1990).
5. C-M. NIU, R. KERSHAW, K. DWIGHT, AND A. WOLD, *J. Solid State Chem.* **85**, 262 (1990).
6. E. F. APPLE, *J. Electrochem. Soc.* **105**, 251 (1958).

7. M. Robbins and M. A. Miksovsky, *J. Solid State Chem.* **5**, 462 (1972).
8. H. Hartmann, *J. Cryst. Growth* **42**, 144 (1977).
9. A. Catano and Z. K. Kun, *J. Cryst. Growth* **33**, 324 (1976).
10. L. S. Lerner, *J. Phys. Chem. Solids* **27**, 1 (1966).
11. W. N. Honeyman, *J. Phys. Chem. Solids* **30**, 1935 (1969).
12. P. C. Donohue and P. E. Bierstedt, *J. Electrochem. Soc.* **121**, 327 (1974).
13. R. Kershaw, M. Vlasse, and A. Wold, *Inorg. Chem.* **6**, 1599 (1967).