OFFICE OF NAVAL RESEARCH

TECHNICAL REPORT NO. 2

Phase Diagram Studies of ZnS Systems

by

J.M. Zhang, W.W. Chen, B. Dunn and A.J. Ardell

Prepared for Publication in

Department of Materials Science and Engineering
University of California, Los Angeles,
Los Angeles, California 90024

September 1, 1988

88 9 16 248

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION		1b. RESTRICTIVE MARKINGS
Unclassified		

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT
	Approved for public release;
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	Distribution unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
No. 2	N00014-87-K-0531

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
University of California, Los Angeles / Bruce Dunn		Office of Naval Research Dr. R. Schwartz

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
Dept. of Materials Science and Engineering University of California, Los Angeles, /CA 90024-1595	Code 3854 Naval Weapons Center China Lake, CA 93555

8a. NAME OF FUNDING / SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO.	PROJECT NO	TASK NO.	WORK UNIT NO

11. TITLE (Include Security Classification)

Phase Diagram Studies of ZnS Systems

12. PERSONAL AUTHOR(S)

J. M. Zhang, W. W. Chen, B. Dunn, A. J. Ardell

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM _____ TO _____	1988/Sept./1	

16. SUPPLEMENTARY NOTATION

To be published in Proc. SPIE Conference on Ceramics and Inorganic Crystals for Optics

17	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The development of infrared-transmitting ZnS-based ceramics with a combination of high strength, hardness and toughness over a range of temperatures is highly desirable. The approach we are currently pursuing is a familiar one to metallurgists, namely the exploitation of thermal, and possibly mechanical, processing of ZnS-base "alloys". Knowledge of the phase equilibria of various ZnS-rich systems is essential to achieve our objectives. Unfortunately, the literature on this subject is sparse, and we have had to undertake such investigations ourselves. This paper describes the results of our initial studies of the solid-state phase equilibria in the ZnS-CdS and $ZnS-Ga_2S_3$ phase diagrams. We also discuss possible processing routes to achieve hard and tough ceramics utilizing the phase diagrams established.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

Phase diagram studies of ZnS systems

J. M. Zhang, W. W. Chen, B. Dunn and A. J. Ardell

Department of Materials Science and Engineering
University of California
Los Angeles, CA 90024

ABSTRACT

The development of infrared-transmitting ZnS-based ceramics with a combination of high strength, hardness and toughness over a range of temperatures is highly desirable. The approach we are currently pursuing is a familiar one to metallurgists, namely the exploitation of thermal, and possibly mechanical, processing of ZnS-base "alloys". Knowledge of the phase equilibria of various ZnS-rich systems is essential to achieve our objectives. Unfortunately, the literature on this subject is sparse, and we have had to undertake such investigations ourselves. This paper describes the results of our initial studies of the solid-state phase equilibria in the ZnS-CuS and ZnS-Ga$_2$S$_3$ phase diagrams. We also discuss possible processing routes to achieve hard and tough ceramics utilizing the phase diagrams established.

I. INTRODUCTION

ZnS has been widely used as an infrared window material because of its good infrared transmission up to 12 μm. However, as a window material, good mechanical properties, especially fracture toughness, thermal shock resistance and erosion resistance are also required. The mechanical properties of single-phase ZnS usually limit its application in many situations. The objective of our research is to enhance the mechanical properties of ZnS, yet retain its good infrared transmission characteristics.

It is well known that the addition of another component to a matrix material can harden it significantly. This can come about simply by solid-solution strengthening or by a composite materials approach if the addition is in the form of a new phase. Alternatively, a combination of thermal and mechanical treatment (e. g. precipitation strengthening) can be employed to introduce and manipulate the dispersion of second phase particles. In any case, the mechanical properties of the material are usually greatly improved. These techniques are already well established for metallic alloy systems and have been used for many years. For instance, precipitation hardening is the principal method of strengthening almost all the wrought aluminum alloys in use today. Transformation toughening of zirconia-based ceramics is another method that exploits the precipitation of particles of a second phase to vastly improve mechanical behavior.

For optical materials it is also necessary to consider the optical properties of the materials after particles of a second phase have been introduced. Care must be taken that the second-phase particles neither absorb nor scatter in the infrared. Absorption losses are controlled by selecting composition systems in which the second phase possesses good infrared transmission. Scattering losses present a more difficult problem. In the present research program, however, the wavelengths of interest are in the range of 10 μm, and the optical losses from scattering can be minimized by keeping the particle size of the second phase much smaller than the wavelength of the incident radiation. Fortunately, small particle sizes are also preferred for improved mechanical properties, often benefitting the strength, fracture toughness and hardness of the ceramic simultaneously. From this perspective, therefore, it is probable that ZnS ceramics can be strengthened by second phase particles, still retaining their good infrared transmission characteristics, if the particle sizes can be controlled such that they are much smaller than the infrared wavelengths involved.

The key to the success of our objective is the choice of a suitable ZnS-based ceramic system, and good candidates must satisfy certain requirements: (1) They should form a solid solution with ZnS at the ZnS-rich end, which will make it possible to solid-solution strengthen or precipitation harden the ceramics; (2) The component material added should be a good infrared-transmitting material itself, otherwise strong absorption might occur; (3) The refractive index of the addition should be close to that of ZnS to avoid substantial scattering losses, although this is not a serious problem if the particles introduced have sizes much smaller than the infrared spectrum.

These objectives can be met, in principle, by manipulation of the composition and thermal treatment of binary ZnS-based ceramic "alloys"; all that is required is an established compilation of binary phase diagrams. Unfortunately, the number

of published phase diagrams involving various sulfides, not to mention zinc sulfide, is surprisingly small. In fact, we were initially aware of only two or three ZnS-metal sulfide phase diagrams despite an exhaustive search of the literature, and these were not really suitable for our purposes. We therefore decided to determine the solid-state phase equilibria of several potentially promising candidate binary systems. The ZnS-CdS and ZnS-Ga$_2$S$_3$ systems were chosen for initial study because they most closely satisfy the criteria stated above.

2. THE ZnS-CdS SYSTEM

CdS possesses excellent infrared transmission properties and the system ZnS-CdS offers considerable promise for developing a two phase microstructure. The ZnS-CdS phase diagram has been the subject of several studies. Ballentyne and Ray[1] investigated ZnS-CdS bulk materials annealed at 1100 °C and found solid solution formation over the complete range of compositions. A study of the phase equilibria in thin films in the ZnS-CdS system has also been reported[2]. For films annealed at 450 °C, Kane et al.[2] found the presence of the wurtzite (hexagonal) and sphalerite (cubic) phases at < 60% and > 85% ZnS, respectively. At intermediate compositions a two-phase region consisting of cubic and hexagonal ZnS solid solutions was observed. These authors did not study the phase equilibria as a function of temperature. A more detailed description of the cubic and hexagonal solid solution boundaries was reported by Kaneko et al.[3] This work, however, was conducted under hydrothermal conditions which are not usually relevant for ceramic processing considerations. As of yet, no results have been presented which accurately map the wurtzite/sphalerite phase boundaries under conditions which are amenable to ceramic processing. A knowledge of this phase boundary is essential if one is to select the proper composition and annealing temperature, and to control the amount of second phase precipitation for two-phase strengthening.
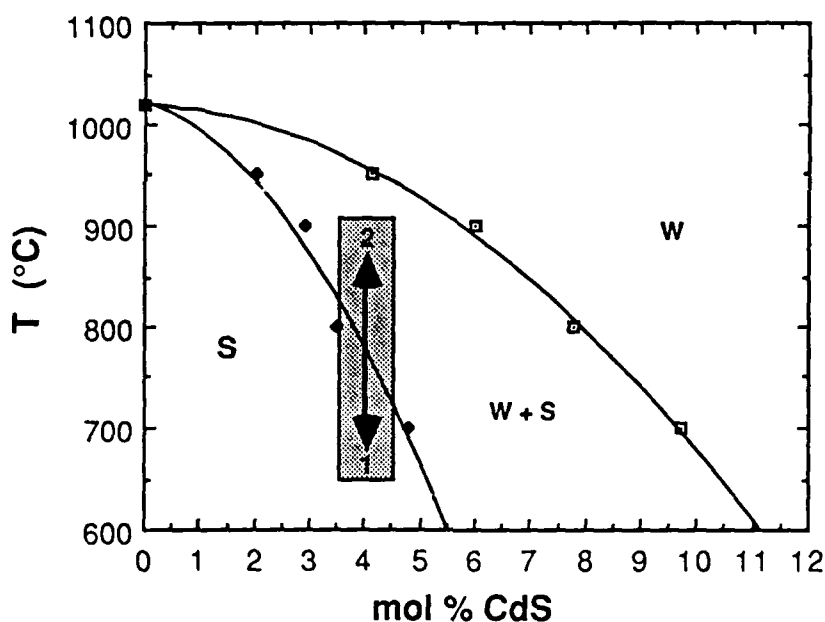

Figure 1. Phase diagram for the ZnS-CdS system in the ZnS-rich region.

The methods we have used to determine the ZnS-CdS phase diagram over the temperature range 700 to 950 °C are described elsewhere[4]. Briefly, the precise compositions of the wurtzite and sphalerite solvuses were determined by lattice parameter measurements and by the disappearing phase method. Both approaches involve the use of X-ray diffraction. A partial phase diagram of the ZnS-rich region is shown in Fig. 1. Some of the more significant features of this diagram are: (1) A range of compositions exists where the sphalerite and wurtzite phases are in equilibrium; (2) The addition of CdS depresses the wurtzite-to-sphalerite transition temperature; (3) The CdS solubility in sphalerite increases as the temperature decreases.

The last finding is particularly noteworthy because alloys which are precipitation strengthened by the classical heat treatment schemes[5] are characterized by having the solute solubility decrease with decreasing temperature. Such behavior is not observed in the ZnS - CdS system, hence a different approach must be utilized for developing the desired two-phase microstructure. One possible route to this end is also depicted in Fig. 1. A dense sample containing ~4 mol % CdS would first be prepared by standard hot-pressing methods[6]. This sample would then be annealed at ~700 °C to form the single phase sphalerite solid solution (point 1 in Fig. 1). A heat treatment at ~900 °C (point 2) would then be made and the wurtzite second phase will nucleate in the cubic solid matrix. Our phase equilibria studies[4] indicate that diffusion in the ZnS matrix is quite slow. Thus, we expect to have considerable control over the nucleation and growth reactions for the wurtzite phase. After heat-treatment, the sample would be rapidly cooled to approximately 600 °C to arrest the precipitation reactions and then slowly cooled to room temperature. Controlled cooling is necessary to prevent thermal shock and, at temperatures below 600 °C, the slow diffusion kinetics ensure that the formation of additional sphalerite solid solution will be minimal.

3. THE ZnS-Ga$_2$S$_3$ SYSTEM

Another series of compositions which display considerable potential for precipitation strengthening with good infrared transmission are in the ZnS-Ga$_2$S$_3$ system. Hahn et al.[7] reported the formation of ZnS solid solutions and the ternary compound, ZnGa$_2$S$_4$ by sintering various compositions of ZnS and Ga$_2$S$_3$. The crystal structure of ZnGa$_2$S$_4$ is tetragonal with lattice constants a = 0.522 nm and c = 1.044 nm. Single crystals of this ternary chalcogenide have also been grown by an iodine vapor transport method[8]. Phase equilibria studies of the Ga$_2$S$_3$-rich end of the ZnS-Ga$_2$S$_3$ system have been reported[9], but the work which is most relevant for our interests is the ZnS-rich portion investigated by Malevskii[10]. These authors found that there was limited solubility of Ga$_2$S$_3$ in ZnS and that a eutectoid reaction involving the decomposition of wurtzite into sphalerite and ZnGa$_2$S$_4$ occurred. The eutectoid contained 19 mol % Ga$_2$S$_3$ and the eutectoid temperature was 810 °C.

The experimental and analytical methods we have used to establish the ZnS-Ga$_2$S$_3$ phase diagram are similar those employed for the ZnS-CdS system[4]. The compositions prepared for this study varied from 3 to 50 mol % Ga$_2$S$_3$ and the temperatures ranged from 700 to 900 °C. An example of how the parametric method is used to determine the sphalerite solvus is shown in Fig. 2. In the single-phase region the lattice constant varies linearly with Ga$_2$S$_3$ content. The compositions of the sphalerite solvus at 700 and 750 °C are indicated by the intersections of the sloping and horizontal lines.
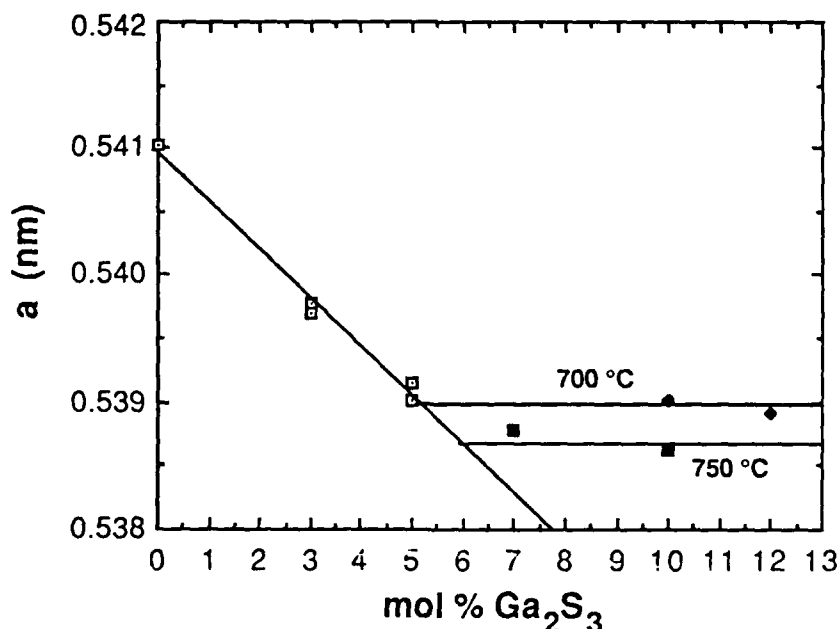

Figure 2. Lattice constant of sphalerite as a function of Ga$_2$S$_3$ content.
The sphalerite solvus at 750 °C is ~6 mol % and that at 700 °C is ~5 mol % Ga$_2$S$_3$.

The phases identified in the present study are superimposed on the phase diagram of Malevskii[10] in Fig. 3 (a). Our initial results indicate that there are discrepancies in the location of the sphalerite solvus and in the composition and temperature of the invariant eutectoid reaction, wurtzite —> sphalerite + tetragonal ($ZnGa_2S_4$). The eutectoid reaction temperature lies between 800 and 850 °C and the eutectoid composition is between 12 and 16 mol % Ga_2S_3. A tentative phase diagram which fits the phase boundaries to our results is shown in Fig. 3 (b). One of the significant features of this phase diagram is that the solute solubility decreases with decreasing temperature (below 800 °C). This behavior is important for achieving precipitation strengthening in metals and alloys[5].
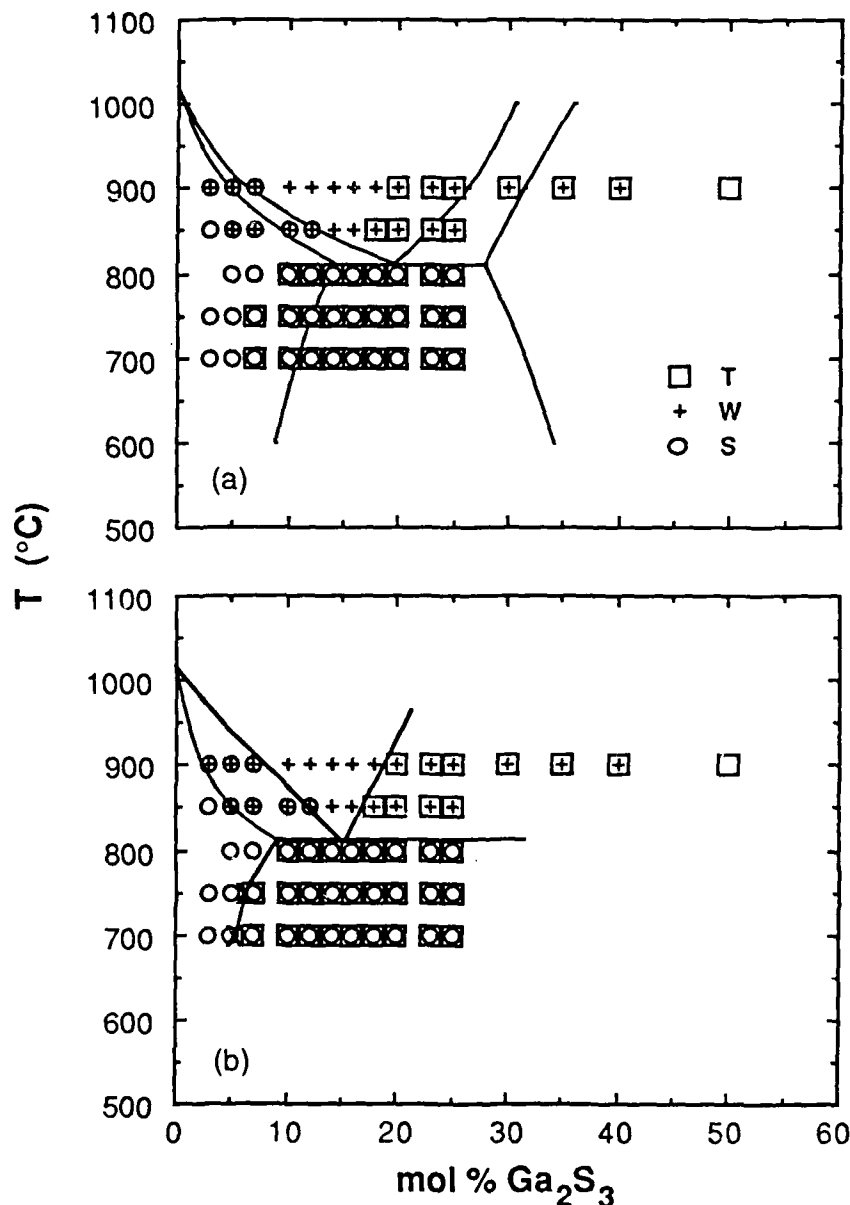

Figure 3. Phase diagrams for the ZnS-Ga_2S_3 system: (a) Data from the present study superimposed on the phase diagram reported by Malevskii[10]; (b) Data from the present investigation. The points at X in (b) represent the values of the solubility limits determined by the intersections of the lines in Fig. 2.

Based on the $ZnS-Ga_2S_3$ phase diagram, there are several types of heat treatments which should lead to strengthening; these are illustrated in Fig. 4. In at least two cases procedures similar to those employed in metals and alloys can be utilized. The first is analogous to precipitation hardening of alloys[5] (path A in Fig. 4). A dense sample containing ~7 mol % Ga_2S_3 would be prepared by hot pressing and then solution treated at 800 °C to produce a single phase sphalerite solid solution. The nucleation and growth of the tetragonal phase, $ZnGa_2S_4$, could then be induced by heating to the aging temperature of ~650 °C. Some of the fundamental issues to be considered are the time at and magnitudes of both the solution treatment and aging temperatures. These processing variables influence such microstructural features as the grain size of the matrix and the size and concentration of the second phase. In this particular example the precipitation of the tetragonal phase could prove interesting because there is excellent matching of the lattice constants of the tetragonal phase with that of sphalerite (a = 0.541 nm).
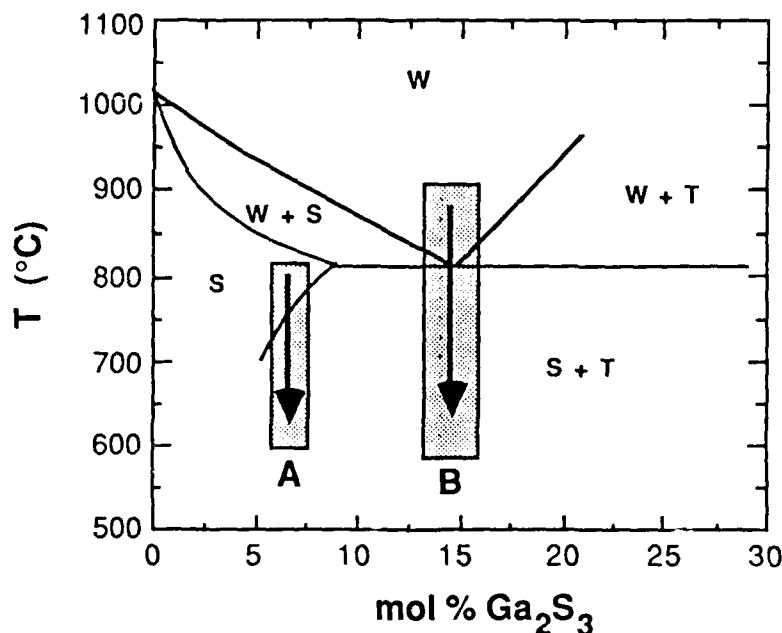

Figure 4. Different heat treatments proposed for strengthening in the $ZnS-Ga_2S_3$ system.
Path A is analogous to precipitation hardening. Path B involves use of the eutectoid reaction.

The eutectoid reaction (path B in Fig. 4) offers an alternative processing means for introducing a second phase. In this case a solid disc (prepared by hot pressing) of the eutectoid composition (~15 mol % Ga_2S_3) would be solution treated to form the equilibrium wurtzite phase. The sample is then heat treated below the eutectoid temperature, where the hexagonal solid solution is expected to decompose to a mixture of the cubic ZnS and tetragonal $ZnGa_2S_4$ phases. The microstructure here is expected to be inherently different from that in path A, and is likely to be lamellar in morphology, which is typical of eutectoid decomposition reactions[11]. This microstructure can, in turn, be modified by selecting compositions which contain somewhat more or less Ga_2S_3 than the eutectoid composition (i. e., hypoeutectoid or hypereutectoid). It is evident, therefore, that the $ZnS-Ga_2S_3$ system offers considerable flexibility with respect to the types of processing treatments available for producing second phases in ZnS matrices.

4. CONCLUSIONS

Although the incorporation of a second phase is well known for improving the mechanical properties of ceramics, such multiphase ceramics are generally undesirable for optical transmission, particularly in the visible. In the present program, however, the wavelengths of interest are in the range of 10 µm and control of the precipitation reactions should present little difficulty in keeping the precipitate diameters much less than this dimension.

The initial part of the research has involved phase equilibria studies of suitable ZnS-based systems. The results derived from these studies are essential because they provide basic information regarding the processing treatments required to manipulate and control the ZnS "alloy" microstructures. The solid-state phase equilibria in these two systems are very different. CdS is very soluble in ZnS and the two-phase microstructure envisioned in this system will be composed of sphalerite and wurtzite solid solutions. Ga_2S_3 exhibits limited solubility in ZnS and the ZnS-Ga_2S_3 system is characterized by a eutectoid reaction. Several different types of thermal treatements are possible in this system; examples are the traditional metallurgical solutionizing anneal followed by a precipitation reaction, and the eutectoid reaction. The diversity of thermal treatments offered by the ZnS-based systems suggests that there will be ample opportunities to develop microstructures which possess enhanced mechanical properties with minimal infrared scattering losses.

5. ACKNOWLEDGEMENT

6. REFERENCES

1. D. W. G. Ballentyne and B. Ray, *Electroluminescence and Crystal Structure in the Alloys System ZnS-CdS*, Physica 27, 337-341 (1961).

2. W. M. Kane, J. P. Spratt, L. W. Hershinger and I. H. Khan, *Structual and Optical Properties of Thin Films of $Zn_xCd_{(1-x)}S$*, J. Electrochem. Soc. 113, 136-138 (1966).

3. S. Kaneko, H. Aoki, Y. Kawahara and F. Imoto, *Solid Solutions and Phase Transformations in the System ZnS-CdS under Hydrothermal Conditions*, J. Electrochem. Soc. 131, 1445-1446 (1984).

4. W. W. Chen, J. M. Zhang, A. J. Ardell and B. Dunn, *Solid-State Phase Equilibria in the ZnS-CdS System*, submitted for publication.

5. A. J. Ardell, *Precipitation Hardening*, Metall. Trans. 16A, 2131-2165 (1984).

6. E. Carnall, Jr., *Hot-Pressing of ZnS and CdTe*, J. Am. Ceram. Soc. 55, 583-583 (1972).

7. H. Hahn, G. Frank, W. Klingler, A.-D. Störger and G. Störger, *Über ternäre Chalkogenide des Aluminiums, Galliums und Indiums mit Zink, Cadmium und Quecksilber*, Z. Anorg. Allg. Chem. 279, 241-270 (1955).

8. R. Nitsche, H. U. Bölsterli and M. Lichtensteiger, *Crystal Growth by Chemical Transport Reactions—I Binary, Ternary, and Mixed-Crystal Chalcogenides*, J. Phys. Chem Solids 21, 199-205 (1961).

9. A. S. Gates and J. G. Edwards, *Vapor Pressures, Vapor Compositions, and Thermodynamics of the $ZnGa_2S_4$-$ZnGa_8S_{13}$ System by the Simultaneous Knudsen and Dynamic Torsion-Effusion Method*, J. Phys. Chem. 82, 2789-2797 (1978).

10. A. Yu. Malevskii, *Ranges of Isomorphic Replacement in the System ZnS-Ga_2S_3*, in Eksp. Issled. Obl. Geokhim. Kristallogr. Redk. Elem., Akad. Nauk SSSR, Inst. Mineral., Geokhim. Kristallogr. Redk. Elem., 12-20 (1967).

11. M. P. Puls and J. S. Kirkaldy, *The Pearlite Reaction*, Metall. Trans. 3, 2777-2796, (1972).