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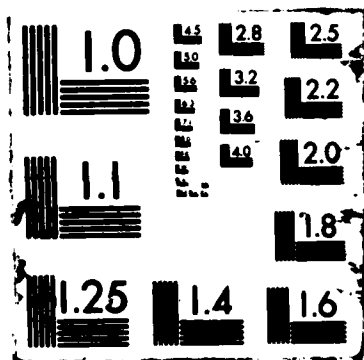
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Preparation and Characterization of Members of the System $(\text{Zn,Se})_{1-x}\text{GaP}_x$

by

H-S. Shen, G-Q. Yao, X-C He, K. Dwight and A. Wold

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PREPARATION AND CHARACTERIZATION OF MEMBERS OF THE
SYSTEM. $(\text{Zn Se})_{1-x}\text{GaP}_x$

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ABSTRACT

Single crystals of members of the system $(\text{ZnSe})_{1-x}(\text{GaP})_x$ were grown by chemical vapor transport using iodine as the transport agent. The IR spectrum of $(\text{ZnSe})_{.905}(\text{GaP})_{.095}$ is not appreciably changed from that of pure ZnSe; however, the hardness and stability towards oxidation are greatly enhanced.

MATERIALS INDEX: II-VI/III-V solid solutions; Infrared transmission.

Introduction

There have been relatively few studies carried out on the preparation and characterization of solid solutions formed between II-VI and III-V compounds. Yim et al. (1, 2) have reported the extent of solid solution between a number of pseudobinary (III-V)-(II-VI) systems and have also grown single crystals using an open-tube vapor-phase epitaxial technique. Sonomura et al. (3) have prepared GaP-ZnS and GaP-ZnSe solid solutions and have reported their photoconducting and photovoltaic properties.

In previous studies of the system $(\text{ZnSe})_{1-x}\text{GaP}_x$ (4,5), it was noted that there was a sharp decrease in the energy gap for compositions close to that of pure GaP. There have been no previous studies of the infrared transmission in any of the members of this system. Pure ZnSe single crystals transmit in the far infrared to 20 microns (6). However, it was observed that this material is extremely soft (7). GaP, on the other hand, is relatively hard although it does not transmit as far in the infrared as ZnSe (8). It was the purpose of this study to investigate the properties of members of the system $(\text{ZnSe})_{1-x}(\text{GaP})_x$ to see if the hardness of ZnSe could be improved and still transmit in the far infrared.

Experimental

Preparation of polycrystalline samples.

Members of the system $(\text{Zn,Se})_{x-n}\text{GaP}_x$ were prepared by the following procedure. Pure zinc (J.M.C. 99.999) was reacted with Se(G&S 99.9995) at temperatures from 500° to 900°C in sealed silica tubes for one week with intermittent grindings to ensure complete reaction. The product was ground and mixed with GaP (Metal Specialties, Fairfield, CT) and slowly heated to 1150°C in

sealed silica tubes for varying periods ranging from 4 to 21 days depending upon the concentration of GaP. The reacted powders were characterized by x-ray diffraction analysis.

Single crystal growth.

Single crystals of members of the system $(\text{ZnSe})_{1-x}\text{GaP}_x$ were prepared by chemical vapor transport using iodine as the transport agent. The appropriate composition of polycrystalline material was introduced into a silica tube which was evacuated to 5×10^{-5} torr. Five mg/cc of iodine were added to the transport tube which was then sealed and the tube set in the back transport mode and run in this mode for two days. Optimum crystal growth occurred when the charge zone was maintained at 1000°C and the growth zone at 965°C . The transport process was carried out for two weeks and the average crystal size was $8\text{mm} \times 5\text{mm} \times 0.5\text{mm}$.

Characterization of products.

Powder diffraction patterns of ground single crystals were obtained with a Norelco diffractometer using monochromatic radiation from a high-intensity copper source ($\lambda\text{-CuK}\alpha_1 = 1.5405\text{\AA}$). Cell parameters were determined from slow-scan ($0.25^\circ/\text{min}$) diffraction patterns over the range $12^\circ < 2\theta < 72^\circ$. Cell parameters were obtained from a least-squares refinement of the data with the aid of a computer program which corrected for the systematic experimental errors.

The microhardness measurements (Knoop indenter) were made on crystals using a Kentron Microhardness Tester. The results given in Table 1 were obtained using a diamond indenter with a 100g load.

The stability of these compounds toward oxidation was determined by heating them in a flowing oxygen stream (65 cc/min) and determining the change in weight during the heating period. The results are shown in Table 1.

Optical and electrical measurements.

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 $2.5 \mu\text{m} - 25 \mu\text{m}$. Transmission through the sample was normalized to the signal obtained in the absence of sample.

Transmission in the vicinity of the optical band edge was measured with an Oriel Model 1724 monochromator, an Oriel G 772-5400 long pass filter, and a calibrated silicon diode detector. Optical band gaps were determined from the responses with and without the crystal in the beam.

The van der Pauw method was used to measure electrical resistivities at 298 K. Contacts were made by the ultrasonic soldering of indium directly onto the samples, and ohmic behavior was established by measuring the current-voltage characteristics.



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TABLE 1
PROPERTIES OF $(\text{ZnSe})_{1-x}(\text{GaP})_x$ CRYSTALS

Nominal (charge) composition (fraction GaP)	Crystal composition** (fraction GaP)	Cubic cell parameter (Å)	Optical energy gap (eV)	Knoop hardness (kg/mm ²)	Stability limit in O ₂ (°C)	Infrared window (μm)
0.0	0.0	5.671(3)	2.66(2)	130(50)	420	2.5-20
0.1	0.068	5.656(2)	2.56(2)	320(50)	460	2.5-20
0.2	0.095	5.650(2)	2.53(2)	320(50)	520	2.5-20
0.4	0.21	5.624(2)	2.47(2)	430(50)	555	2.5-20*
0.6	0.26	5.614(2)	2.43(2)	440(50)	610	2.5-20*
1.0	1.00	5.451(2)	2.28(2)	900(50)	> 900	2.4-14

** Obtained from plot of cell parameter versus composition of polycrystalline standards.

* There is a weak absorption band at 14μm.

Results and Discussion

Single crystals of members of the system $(\text{ZnSe})_{1-x}(\text{GaP})_x$ were grown by chemical vapor transport using iodine as the transport agent. From the cell parameters vs chemical composition for polycrystalline materials, a standard plot was drawn. The composition of crystals grown by chemical vapor transport was determined from this plot after the cell parameters were measured. The results of these determinations are given in Table 1. It can be seen that the transported crystals contain far less GaP than the original charge. Crystals were therefore grown containing up to almost 30 mole percent GaP and pure GaP. Catalano et al. (4, 5) succeeded with the growth of crystals containing from up to 82 mole percent GaP to pure GaP. The indirect optical band gaps were obtained from plots of $(\alpha h \nu)^{1/2}$ vs energy and are also given in Table 1. The measured energy gap decreases from 2.66 eV for ZnSe to 2.28 for pure GaP. All of the crystals gave resistivities greater than $10^8 \Omega\text{-cm}$. The plot of hardness vs composition shown in Fig. 1 indicates that there is additional hardness obtained to that expected from ZnSe samples containing between 6.8 and 26 mole percent GaP.

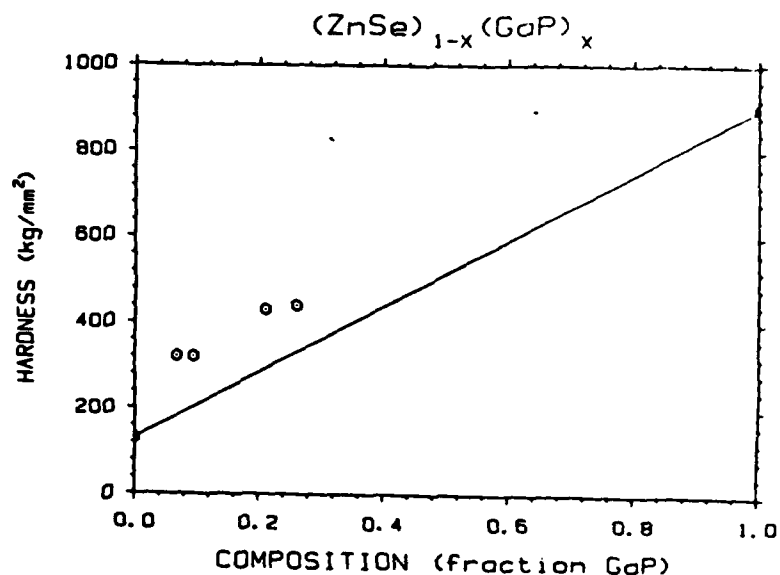


Fig. 1. Variation of hardness with composition in the system $(\text{ZnSe})_{1-x}(\text{GaP})_x$.

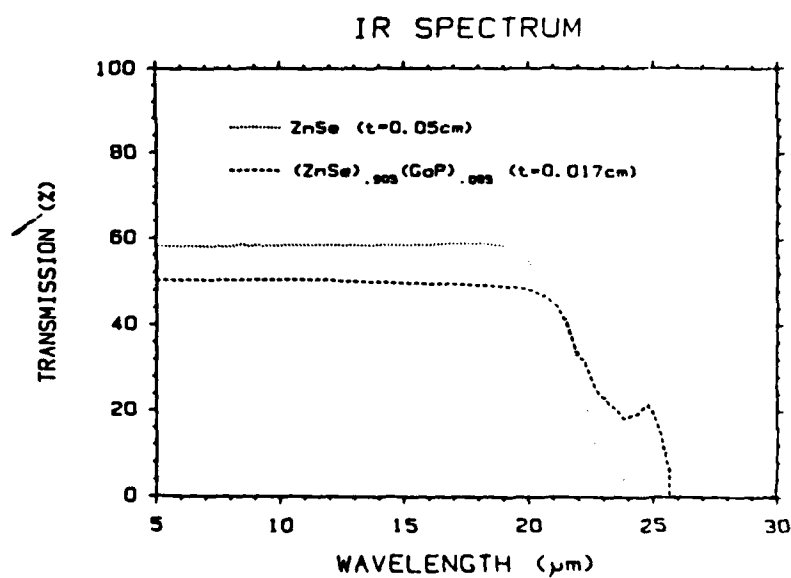


Fig. 2. Infrared transmission of $(\text{ZnSe})_{0.905}(\text{GaP})_{0.095}$ compared with that of pure ZnSe.

The loss in weight on heating samples in flowing oxygen indicates that there is an increase in the stability of products with the measured GaP content. Crystals containing 26 mole percent GaP did not begin to lose weight until they were heated to over 600°C. It can also be seen from Table 1 that the addition of almost 10 mole percent of GaP to ZnSe does not change the IR transmission range. A plot of the IR spectrum is given for $(\text{ZnSe})_{.905}(\text{GaP})_{.095}$ in Fig. 2 and is compared to pure ZnSe. It is interesting to note that whereas the IR spectrum of ZnSe is not appreciably changed at this composition of GaP, the hardness and stability towards oxidation are greatly enhanced.

Acknowledgments

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