

Crystal Growth and Characterization of the Solid Solution (ZnSe)_{1-x}(CuMSe₂)_x (M=Al, Ga, or In)

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Single crystals of (ZnSe)_{1-x}(CuMSe₂)_x (M=Al, Ga, or In) were grown by chemical vapor transport technique. Powdered polycrystalline samples of (ZnSe)_{1-x}(CuMSe₂)_x (M=Al, Ga, or In) were also prepared by the direct combination of the elements. The chemical composition of these single crystals was determined by comparing their lattice parameters with those of the standard polycrystalline samples. The IR transmission range of single crystals of (ZnSe)_{1-x}(CuMSe₂)_x (M=Al, Ga, or In) is slightly narrower than that observed for pure ZnSe. However, these materials still show good transmission in the long-wavelength IR range. The addition of small amounts of CuMSe₂ (M=Al, Ga, or In) considerably increases the hardness of ZnSe.

Introduction

ZnSe crystallizes with cubic zincblende structure (space group *F*43m). The physical properties of ZnSe have been studied extensively because it offers a variety of unique device applications. It can be used as IR window materials because of its wide transmission range in the far-infrared. However, ZnSe is relatively soft, which limits its suitability for the application of IR window.¹⁻³

Several studies for the metal doped ZnSe systems or the alloy of (ZnSe)_{1-x}(GaP)_x have been carried out to overcome the softness of ZnSe.¹⁻⁵ It was claimed that several compounds in the systems of Zn_{1-x}Ni_xSe, (GaP)_x(ZnSe)_{1-x}, Zn_{1-x}Fe_xSe, and Zn_{1-x}Co_xSe gave similar infrared spectra to pure ZnSe, if the value of *x* < 0.1. It has also been reported that spectroscopic studies of the single crystals of (ZnS)_{1-x}(CuMS₂)_x (M=Al, Ga, or In) showed similar IR absorption properties to pure ZnS and they are much harder than ZnS.^{6,7} In this work, it was intended to prepare and characterize the (ZnSe)_{1-x}(CuMSe₂)_x (M=Al, Ga, or In) single crystal systems in order to improve the hardness of ZnSe without deteriorating the optical properties. In contrast, only a few studies have been carried out on the preparation and characterization of solid solutions between ZnSe and CuMSe₂ (M=Al, Ga, or In).⁸⁻¹⁰ The ternary selenide chalcogenides (I-III-VI₂; I=Cu, III=Al, Ga, or In, and VI=Se) crystallize with tetragonal chalcopyrite structure. In this structure, there is a tetragonal ordering of Cu(I) and M(III) (M=Al, Ga, or In) ions on the cation sites in zincblende, which results in a doubling of the *c*-axis. V.G. Lambrecht, Jr. and P.C. Donohue *et al.* have studied the cell dimensions and structures of the selenide chalcopyrite-ZnSe pseudo-binary systems.^{8,9} They reported that CuMSe₂ (M=Al, Ga, or In) members were totally miscible with ZnSe, because of their similarity in the crystal structure and unit cell dimension. In the solid solution of ZnSe-CuGaSe₂ system, the cubic zincblende structure can be retained for up to 40 mole% of CuGaSe₂, while that in the solid solution of ZnSe-CuInSe₂ system can be formed for up to 30 mole% of CuInSe₂. Donohue *et al.* reported that a complete solid solution between ZnSe and CuAlSe₂ could be formed until the substitution of CuAlSe₂ is up to 33 mole%.⁹

The chemical vapor transport method has been widely and conveniently applied to grow single crystals of ZnS, ZnSe, CuMS₂, and CuMSe₂ (M=Al, Ga, or In), since it requires relatively lower reaction temperature than the direct melt method does.¹⁻⁷ In this study, the single crystals of (ZnSe)_{1-x}(CuMSe₂)_x (M=Al, Ga, or In) were grown by chemical vapor method and their physical properties were studied. Several compositions of polycrystalline samples were also prepared by the direct combination of elements, and were used for the evaluation of the actual compositions of the prepared single crystals.

Experimental

Preparation of polycrystalline sample. Members of the systems (ZnSe)_{1-x}(CuMSe₂)_x (M=Al, Ga, or In) were prepared by the following procedure. Polycrystalline samples with different compositions were prepared by using stoichiometric amount of zinc (Gallard and Schlesinger 99.9995%) sublimed prior to use, copper (Johnson Matthey 99.999%) pre-reduced in Ar/H₂ (85/15), aluminum (Jarrel-Ash 99.999%), gallium (Johnson Matthey 99.999%), indium (Johnson Matthey 99.9995%) and selenium (UMC 23333, 99.999%). Appropriate weights of the reactants to give a total weight of 2 g of products were sealed in evacuated cylindrical silica tubes (inner diameter: 12 mm, length: 60 mm). In order to complete the reaction between the metal and selenium without explosion of the sample tubes, the tubes were heated consecutively 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 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 slowly down to room temperature in the furnace.

Crystal growth. Single crystals of ZnSe and (ZnSe)_{1-x}(CuMSe₂)_x (M=Al, Ga, or In) were grown by chemical vapor transport using iodine as the transport agent. Polycrystalline samples were introduced into a silica tube (inner diameter: 12 mm, length: 300 mm), which had been previously heated close to their melting point in order to minimize the number

Table 1. Growth Conditions for Single Crystals of Solid Solutions $(\text{ZnSe})_{1-x}(\text{CuMSe}_2)_x$ ($M=\text{Al, Ga, or In}$, $x=0.05$ or 0.10) and Crystal Sizes

Species of M	Nominal composition (x)	Charge temperature (°C)	Growth temperature (°C)	Crystal size (mm)
—	0.00	850	805	8×5×2
Al	0.05	800	755	6×4×4
	0.10	800	755	7×4×3
Ga	0.05	800	755	8×4×3
	0.10	800	755	6×5×3
In	0.05	790	760	6×3×2
	0.10	790	760	7×3×2

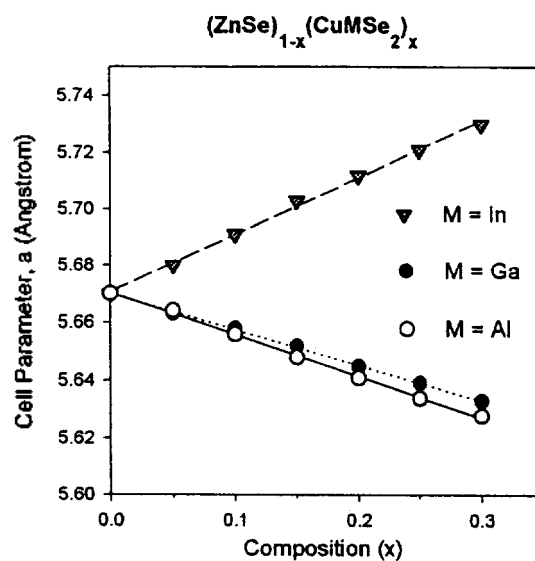
of nucleation site. The tube was evacuated up to 10^{-5} torr and freshly sublimed iodine (Deepwater Chemical Co., Std. ACS reagent 99.9%) was introduced as transport agent at a concentration of 5 mg/ml. The tube was sealed off and enclosed in a tightly wound Kanthal coil (to even out temperature gradients) and the whole assembly was placed in a three zone furnace. The temperature program for crystal growth consisted of setting the furnace to back transport mode for one 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.¹¹ The optimum crystal growth for ZnSe can be achieved when the charge zone was kept at 850°C and the growth zone at 805°C . The optimum growth conditions for single crystals of $(\text{ZnSe})_{1-x}(\text{CuMSe}_2)_x$ ($M=\text{Al, Ga, or In}$) ($x=0.05$ or 0.10) were summarized in Table 1. The transport process was carried out for 7 days for ZnSe and $(\text{ZnSe})_{1-x}(\text{CuMSe}_2)_x$ ($M=\text{Al, Ga, or In}$) ($x=0.05$ or 0.10). The typical sizes of prepared single crystals with different compositions are also given in Table 1.

Characterization of products. X-ray powder diffraction patterns of the samples were obtained using Philips diffractometer and monochromated high intensity Cu $K_{\alpha 1}$ radiation ($\lambda=1.5405 \text{ \AA}$). For the determination of cell parameters, diffraction patterns were taken over the range of $12^\circ < 2\theta < 80^\circ$ with a scan rate of $0.25^\circ/2\theta/\text{min}$. Precise lattice parameters were obtained from the diffraction peaks using a least squares refinement program which corrects for the systematic errors of the diffractometer.^{12,13}

Selected single crystals were polished progressively with the suspensions of 1, 0.3 and $0.05 \mu\text{m}$ alumina on alpha A polishing cloth (Mark V Laboratory) using a minimet polisher. The optical measurements were performed at room temperature with a Perkin-Elmer 580 double scanning infrared spectrophotometer. The measurements were carried out in the transmission mode over the range $2.5\text{--}50 \mu\text{m}$.

Microhardness measurement were performed using the polished single crystals with a Kentron microhardness tester (Knoop indenter). The results were obtained using a diamond indenter with 25 g load for ZnSe and $(\text{ZnSe})_{1-x}(\text{CuMSe}_2)_x$ ($M=\text{Al, Ga, or In}$).

The stability of these compounds toward oxidation was evaluated by using the laboratory-made TGA balance. The ground crystal samples in the TGA bucket were slowly heated up in a flowing oxygen atmosphere (heating rate: 2°C

**Figure 1.** Variation of Cell Parameters of $(\text{ZnSe})_{1-x}(\text{CuMSe}_2)_x$ [$M=\text{Al, Ga, or In}$] with the Concentration of CuMSe_2 .

/min, oxygen flow rate: 60 ml/min) and the weights of samples were monitored during the heating process. The decomposition temperature was regarded as the temperature where the weight of sample began to change.

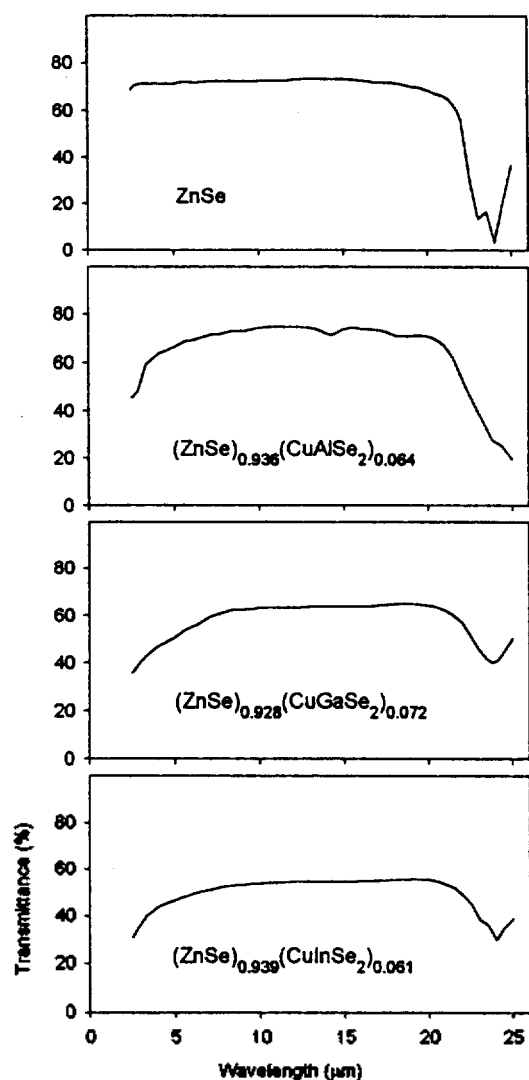
Results and Discussion

X-ray diffraction patterns indicates that $(\text{ZnSe})_{1-x}(\text{CuMSe}_2)_x$ ($M=\text{Al, Ga, or In}$) polycrystalline samples are single phases and crystallize with cubic zincblende structure for up to 30 mole% of CuMSe_2 ($M=\text{Al, Ga, or In}$). In Figure 1, the cell parameters were plotted as a function of chalcopyrite concentration. When the chalcopyrite concentration is lower than 30 mole%, the cell parameters were decreased linearly with increasing the amount of substituted chalcopyrite for the aluminum and gallium system, and were increased linearly for the indium system. They are in accordance with Vegard's law and are in good agreement with those reported by previous papers.⁴⁻⁶ In this work, these cell parameter data were used to evaluate the composition of crystal samples. The actual doping level in the single crystals of $(\text{ZnSe})_{1-x}(\text{CuMSe}_2)_x$ ($M=\text{Al, Ga, or In}$) ($x=0.05$ or 0.10), grown by chemical vapor transport, were determined by comparing their cell parameters with those obtained from the plot of cell parameters vs. composition for the standard polycrystalline samples, as shown in Figure 1. The evaluated compositions for $(\text{ZnSe})_{1-x}(\text{CuMSe}_2)_x$ ($M=\text{Al, Ga, or In}$) crystals are presented in Table 2. It is noted that the actual composition of the prepared crystals is deviated from their nominal composition. This indicates that the transport efficiency of aluminum and gallium by iodine gas is lower than that of zinc, while indium shows similar efficiency.

The hardness values, determined by the Knoop method, are given in Table 2. The measured hardness of pure ZnSe is 120 kg/mm^2 , which is in good agreement with previous reports.^{12,5} It is found that the micro-hardness of chalcopyrite doped ZnSe crystals is doubled compared to that of pure ZnSe, and all of three samples display similar hardness val-

Table 2. Properties of $(\text{ZnSe})_{1-x}(\text{CuMSe}_2)_x$ ($M=\text{Al, Ga, or In}$) Single Crystals

Species of M	Nominal composition (x)	Actual composition (x)	Cell parameter (\AA)	Knoop hardness (Kg/mm^2)	Decomposition Temp. ($^{\circ}\text{C}$)	Transmission range (μm)
—	0.0	0.0	5.670	120	420	2.5-20
Al	0.05	0.036	5.666	220	365	4.0-13.5
	0.10	0.067	5.661	230	355	4.0-13.5
Ga	0.05	0.040	5.665	220	420	5.0-20
	0.10	0.072	5.671	250	420	5.0-20
In	0.05	0.060	5.683	210	410	5.0-20
	0.10	0.105	5.693	220	425	5.0-20

**Figure 2.** IR Spectra of ZnSe and Ternary Chalcogenide Single Crystals; Thickness of Crystal: 0.02 cm.

ue, regardless of dopant species. These trends are in accord with those of the sulfide systems of $(\text{ZnS})_{1-x}(\text{CuMS}_2)_x$ ($M=\text{Al, Ga, or In}$).^{6,7} The thermal stability data, taken in a flowing oxygen atmosphere, show that the onset temperature of decomposition, for the ZnSe-CuGaSe_2 and ZnSe-CuInSe_2 systems, is similar to that of pure ZnSe. On the other hand, the introduction of CuAlSe_2 decreases the thermal stability of ZnSe. These stability data indicate that the introduction

of small amount of chalcopyrite does not increase the bond strength of ZnSe-CuMSe_2 systems. XRD data also show that a small amount of chalcopyrite dopant does not alter the zincblende structure of ZnSe. Nonetheless, it is noted that the microhardness of pure ZnSe are significantly improved by the doping of chalcopyrite. In the ZnSe-CuMSe_2 systems, the lattice structure is basically constructed with cubic zincblende, but the metal atoms constructing the each unit cell are not identical. Therefore, it is considered that the great increase of micro-hardness is originated from the local distortion of ZnSe structure, with the doping of foreign elements in different sizes.

The IR transmission data summarized in Table 2 are plotted in Figure 2. It is indicated that pure ZnSe transmits in the range of 2.5-20 μm . This value is in good agreement with previous reports.^{1,2} The infrared spectral response for single crystals of chalcopyrite doped ZnSe exhibits that their transmission ranges are slightly reduced compared with that of pure ZnSe. Kaminow *et al.* reported that 9 vibrational modes are infrared active out of 21 lattice vibration modes in chalcopyrite structure, while only one mode is infrared active in ZnSe.¹⁴ It is deduced that these complex infrared active vibrational modes in chalcopyrite structure reduce the transmission range of chalcopyrite doped ZnSe crystal in the far infrared range. In the $\text{CuAlSe}_2\text{-ZnSe}$ system, there is a weak absorption band at 13.5 μm . It comes from the Al-Se bond, which has a relatively small reduced mass compared with Zn-Se bond in the zinc selenide system. In Figure 2, $\text{CuInSe}_2\text{-ZnSe}$ system shows a low transmittance compared to other systems, but the reason is not clear at this moment. On the other hand, the CuGaSe_2 -doped ZnSe crystal shows a relatively high and constant transmittance level over the 5-20 μm spectral range, and it is considered to be a promising candidate for the application of IR window material.

Conclusion

It is clearly seen that the improvement of microhardness of ZnSe can be attained by doping a small amount of CuMSe_2 ($M=\text{Al, Ga, or In}$) into ZnSe crystals. The infrared spectral responses for single crystals of CuMSe_2 doped ZnSe ($M=\text{Al, Ga, or In}$) exhibit that their transmission ranges are slightly reduced compared with that of pure ZnSe. But, these materials still show good IR transmission at the 5-20 μm range. Among the three chalcogenide-doped ZnSe systems studied in this work, CuGaSe_2 -doped ZnSe crystal appears to be the best candidate for the application of IR window material from the consideration of optical property.

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The Influence of Protecting Groups on the β -Sheet Structure Stability of Protected Peptides¹⁾

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The influence of protecting groups on the β -sheet-structure-stability of protected peptides was studied in organic solvents. α -amino groups, carboxyl groups and side chain functional groups of model peptides were protected by suitable groups commonly used in peptide synthesis. The difference of the solubilities of model peptides was investigated by the solvent-titration method by using IR absorption spectra. The β -sheet structure of model peptide in CH_2Cl_2 was easily disrupted by increasing the amounts of DMSO. The β -sheet-structure-stabilizing potentials of each protecting group showed similar behaviors except Npys, Mts and Z₂. The result exhibits that the $\langle\text{SP}_\beta\rangle$ values of protected peptides are almost independent of the kinds of their protecting groups.

Introduction

The insolubility of protected peptides in organic solvents is one of the most serious obstacles in peptide and protein syntheses. The insolubility is due to intermolecular hydrogen-bonded β -sheet aggregation. The disruption of the β -sheet structure by sufficient solvation of a peptide chain is important in carrying out the successive coupling reactions smoothly. Thus, the evaluation of the β -sheet structure stability of protected peptides is essential for the design of synthetic routes for peptides and proteins. The most important thing in selecting the appropriate solvent and deciding of synthetic route is to expect the solubility of protected peptide, and this is connected directly with the stability of β -sheet structure.

In previous paper,^{2,3} we proposed a predictive method for the solubility of protected peptides. The prediction was carried out by using the β -sheet structure stabilizing potentials, SP_β , of the 20 kinds of amino acid residues in protected peptides whose side-chain functional groups were protected by suitable groups commonly used in peptide synthesis.

Using model host-guest peptide, the β -sheet structure of protected peptides in CH_2Cl_2 was disrupted by increasing the amounts of DMSO. The disrupting behaviors were dependent on the nature of the guest amino acid residues. According to these results, the 20 guest amino acid residues could be classified into six groups. Arg(Mts), Val, Asn, Gln, Gly, Ala, His(Bom), Ile have high β -sheet structure formation ability, Phe, Trp(CHO), Tyr(Bzl), Cys(Bzl), Lys(Z), Glu(OBzl), Met(O) have average ability, and Ser(Bzl), Thr(Bzl), Asp(OBzl), Pro have low ability.

The evaluation of the β -sheet-structure stability of the protected peptides was performed by calculating their $\langle\text{SP}_\beta\rangle$ values, which are defined as the arithmetic average of the β -sheet-structure-stabilizing potentials, SP_β , of the amino acid residues composing the protected peptides. Using 77 kinds of protected tri- to heptapeptide fragments of *E. coli* ribosomal protein L7/L12, we showed that their $\langle\text{SP}_\beta\rangle$ values are useful for the estimation of their β -sheet-structure-stability in organic solvents.⁴ The protected peptides mentioned above were protected as follows: α -Amino groups are protected by Boc, carboxyl groups are protected by Pac and side chain