JOURNAL OF MATERIALS SCIENCE **33** (1998) 183–188

The $Ag_xCu_{1-x}InS_2$ solid solutions with $0 \leqslant x \leqslant 1$

I. V. BODNAR, L. V. YASYUKEVICH
Belarus State University of Information Science and Radio Electronics, 6 P. Brovki, Minsk 220069, Belarus
B. V. KORZOUN
Institute of Physics of Solids and Semiconductors, 17 P. Brovki, Minsk 220072, Belarus
A.G. KAROZA
Institute of Molecular and Atomic Physics, 70 F. Skoriny, Minsk 220072, Belarus

The phase equilibriums in the $AgInS_2$–$CuInS_2$ system were investigated by means of X-ray diffraction and differential thermal analysis and the $AgInS_2$ and $CuInS_2$ ternary compounds and the $Ag_xCu_{1-x}InS_2$ solid solutions were grown by two-zone horizontal method with the following directed crystallization of melt. The T–x phase diagram of this system was constructed and the formation of solid solutions in the complete range of compositions was discovered. The composition dependencies of microhardness, transmission spectra in the range of the fundamental absorption, infrared transmission spectra in the range from 150 to 400 cm^{-1} for the $Ag_xCu_{1-x}InS_2$ solid solutions were investigated. It was discovered that the composition dependence of microhardness is expressed by smooth curve having maximum for $x = 0.2$. The composition dependencies of band gap have been analytically expressed at 77 and 293 K for the $E \perp c$ and $E \parallel c$ direction of polarization and have non-linear behaviour. From the studies of the infrared transmission spectra the frequencies of optical phonons were determined and it was discovered that their composition dependence shows single mode behaviour.

1. Introduction

The ternary semiconducting compounds of the I–III–VI_2 group (I – Cu, Ag; III – Al, Ga, In; VI – S, Se, Te) were sintered and investigated by X-ray method for the first time in the paper [1]. These are prospective materials for detectors and sources of radiation, solar cells, optical filters and other devices of optoelectronics. The compounds of this group, $AgInS_2$ and $CuInS_2$, attract great attention because of the possibility of fabrication of light-emitting diodes of linear-polarized radiation and solar cells with high efficiency [2–4]. These compounds have been widely studied, but the information about their solid solutions $Ag_xCu_{1-x}InS_2$ is rather scarce. The only work is by Robbins *et al.* [5] where three alloys with $x = 0.25$, 0.5 and 0.75 were prepared and a conclusion about the formation of the complete series of solid solutions in the $AgInS_2$–$CuInS_2$ system has been made.

The aims of this paper are: (i) the preparation of alloys of the $AgInS_2$–$CuInS_2$ system and their crystal growth; (ii) the construction of T–x phase diagram of this system by differential thermal analysis (DTA) and X-ray diffraction; (iii) the measuring of optical transmission and determination of energy gaps; (iv) the study of the infrared transmission spectra in the range from 150 to 400 cm^{-1}; (v) the investigation of the microhardness and its composition dependence.

2. Preparation of samples and experimental procedure

To obtain the $AgInS_2$ and $CuInS_2$ ternary compounds and their solid solutions copper of 99.999% purity, argentum (99.999%), indium (99.999%) and sulphur (99.9999%) were used. Sulphur was additionally purified by sublimation. The elements were weighed to be about 20 g in total according to the molar ratio of the corresponding ternary compound or solid solution. Then they were sealed in a double quartz tube of about 20 cm in length under a vacuum of $\sim 1 \times 10^{-3}$ Pa. The quartz ampoules were placed into one zone electric furnace of the tube type. At the first stage the temperature was increased to 770 K with rate of 50 K h^{-1}. The second stage was the maintenance of this temperature simultaneously with the vibrational mixing of ampoule and its content during 3 h. The third stage was the increasing of temperature with the same rate to 1370 K for the alloys with $x = 0$–0.5 and to 1270 K for the alloys with $x = 0.5$–1. After these procedures the melt was kept during 3 h with its vibrational mixing. The final stage was the decreasing of temperature with rate of 100 K h^{-1} to the room temperature. The homogeneous annealing of these alloys was performed at 1070 K for $0 \leqslant x \leqslant 0.5$ and at 870 K for $0.5 < x \leqslant 1$. The resulting ingots were homogeneous polycrystals alloys that was established by X-ray diffraction and chemical analysis.

TABLE I Results of chemical analysis of the $Ag_xCu_{1-x}InS_2$ solid solutions (in mass %)

X (molar part)	Ag		Cu		In		S	
	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.
0	–	–	26.20	25.89	47.30	46.81	26.45	26.54
0.1	4.37	4.32	23.16	23.20	46.50	46.95	25.97	25.88
0.3	12.65	12.35	17.39	17.58	44.89	44.50	25.07	25.20
0.5	20.38	20.49	12.01	11.77	43.38	43.66	24.23	24.40
0.7	27.61	27.37	6.97	6.54	41.98	42.60	23.44	23.80
0.9	34.38	34.70	2.25	2.63	40.66	40.33	22.70	22.64
1	37.61	37.84	–	–	40.03	39.67	22.36	22.06

Composition of compounds and their solid solutions was established by chemical analysis. Copper and argentum were determined by the extraction photometry method using natrium dietilcarbonate [6, 7]. The content of indium was measured by photometry method [8] using xilenum orange as reagent, and the content of sulphur was estimated by complexonometric method [9]. The relative error of determination of content of these elements does not exceed 5% for photometry method and 2% for complexonometric method. The experimental results of chemical analysis are coincided with the calculated ones and are given in Table I.

Homogeneity of the alloys of the $AgInS_2$–$CuInS_2$ system was determined by X-ray diffraction method. The angle position of diffraction peaks was measured using DRON-2 apparatus (CuK_α-radiation, Ni filter). The investigations were made on powders of samples prepared according to above mentioned technique. To liquidate the mechanical strains the additional heat annealing of these powders in vacuum at 600 K during 2 h was performed. Only series of diffraction lines corresponding to the tetragonal chalcopyrite structure were presented. Homogeneity of solid solution was also confirmed by resolution of high angle lines.

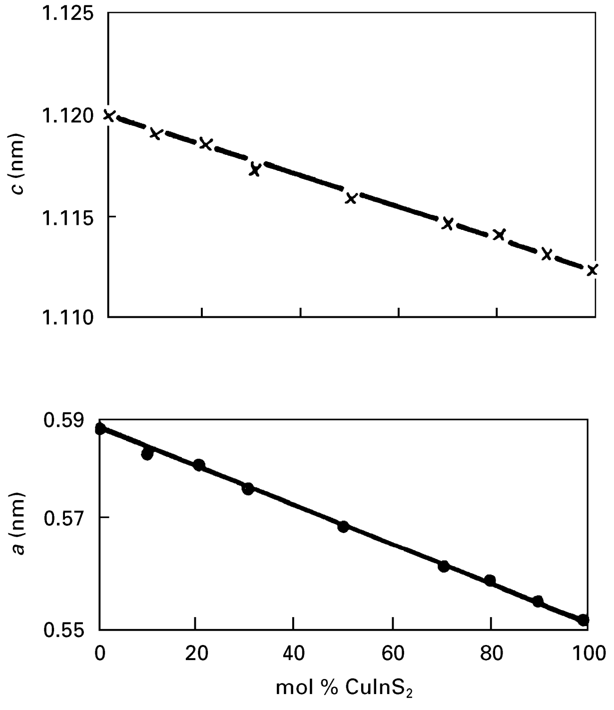

Figure 1 The composition dependence of the *a* and *c* lattice constants in the $AgInS_2$–$CuInS_2$ system.

The measured diffraction angles allow to calculate the *a* and *c* lattice constants. Fig. 1 presents the composition dependence of these constants that is constructed on the base of chemical and X-ray diffraction results. Their change is accomplished according to Vegard's rule.

3. Results and discussion

3.1. *T*–*x* phase diagram of the $AgInS_2$–$CuInS_2$ system

The phase equilibriums in the $AgInS_2$–$CuInS_2$ system were investigated by means of X-ray diffraction and differential thermal analysis. To take the thermograms the obtained ingots were crushed and the part of powder of ~2 g was placed into evacuated quartz vessels. The phase transformation temperature was measured by a platinum/platinum–rhodium thermocouple calibrated using the reference materials in the range from 373 to 1573 K. Since the investigated substances can decompose at temperatures lower than the melting temperatures, then to prevent their dissociation the vessels were filled with the quartz ballast so that no free space was left. Annealed aluminium oxide was used as a reference material. The heating rate was established by thermoregulator from 3 to 5 K min^{-1}. The temperatures of the phase transformations were determined from both the heating and cooling curves, the difference between them being 3 K.

The investigations for $AgInS_2$ showed two thermal effects at 958 and 1145 K, corresponding to the solid state transformation from chalcopyrite (α) to rhombic (β) structure and melting respectively. There are three thermal effects at 1248, 1313 and 1363 K on the thermograms of $CuInS_2$. According to the proposals of Palatnik *et al.* [10] and our data [11] these thermal effects correspond to solid state transitions from chalcopyrite (α) to sphalerite (γ) structure (1248 K), presumably from sphalerite to wurtzite (δ) structure (1313 K), and melting (1363 K).

Fig. 2 gives the *T*–*x* phase diagram of the $AgInS_2$–$CuInS_2$ constructed by means of X-ray diffraction analysis and DTA. This diagram has a complex look. Solid state transformation from chalcopyrite structure to rhombic one is observed for the alloys with 0–30 mol % of $CuInS_2$.

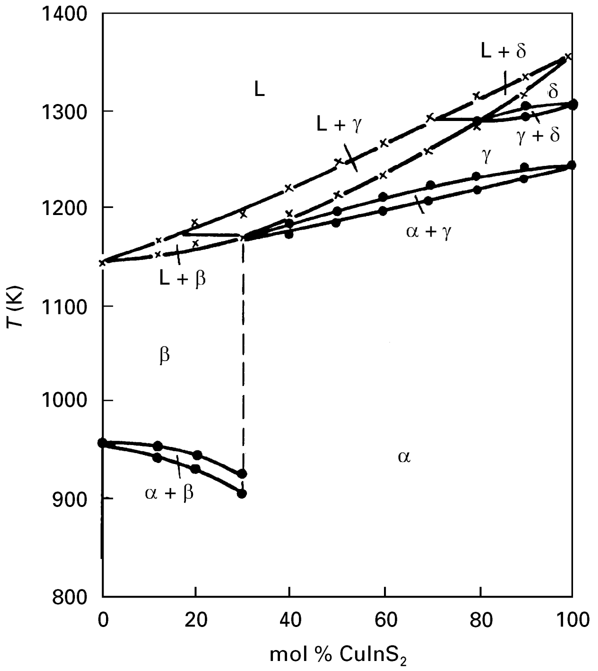

Figure 2 The T–x phase diagram of the $AgInS_2$–$CuInS_2$ system.

These results allow us to make the following conclusions. First of all it is seen that the complete series of solid solutions is formed in this system. In the second place the knowledge of phase diagram allow to work out methods of crystal growth of the $Ag_xCu_{1-x}InS_2$ solid solutions.

3.2. Crystal growth

The $AgInS_2$ and $CuInS_2$ ternary compounds and the $Ag_xCu_{1-x}InS_2$ solid solutions were grown by two-zone horizontal method with the following directed crystallization of melt. Metallic components in corresponding ratio were loaded in a quartz boat and then placed into a quartz ampoule. Sulphur was kept in the opposite end of ampoule. This amount allows the vapour pressure to reach 2.026–3.039×10^5 Pa. Then the ampoule was evacuated and placed into a two-zone horizontal electric furnace. The boat with the metallic components was kept in the hot zone where the temperature was higher than 20–30 K above the melting point of the corresponding alloy. The temperature of the cold zone was increased gradually to 700–720 K, held during 2 h to react metallic components with sulphur vapours. Then the temperature was increased to 750–800 K and held during 1 h to complete the reaction. After that the directed crystallization of melt with rate 2–3 K h^{-1} was realized. To homogenize obtained alloys, they were annealed at 870 K for the solid solutions with $0.3 \leqslant x \leqslant 1$ and 1070 K for the solid solutions with $0 \leqslant x < 0.3$ for 720 h. According to this method the single crystals of the $Ag_xCu_{1-x}InS_2$ solid solutions with crystal grain dimensions $6 \times 3 \times 2\,mm^3$ were grown. The composition of the obtained crystals was determined taking into account the validity of Vegard's law.

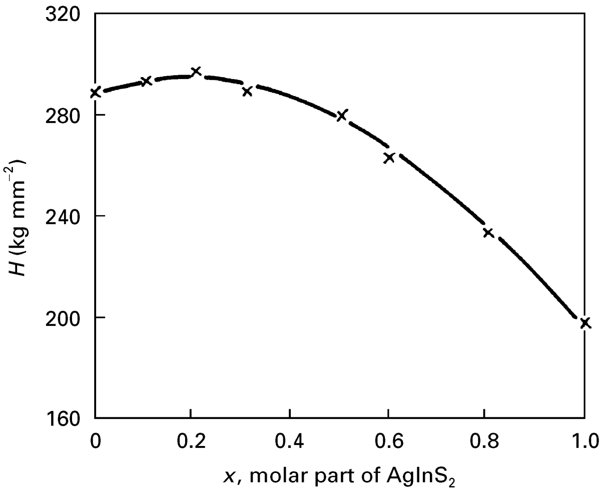

Figure 3 The composition dependence of microhardness of the $Ag_xCu_{1-x}InS_2$ solid solutions.

3.3. Microhardness

The studies of microhardness were carried out in the (1 1 2) plane on crystal grains. The ingots were oriented and cut into plates, polished and lapped from one side, etched in a special etchant (mixture of HNO_3 and H_2SO_4 acids with adding $Bi(NO_3)_3$). The microhardness was measured on a PMT-3 apparatus, the strength being 0.2 N. The imprints developed cracks when large forces were applied which made it necessary to take into account the microcracks. Because no regularities in the change of the microcracks were observed, only the imprints without cracks were taken into account. The value was calculated as arithmetical mean from 15–20 imprints, using the well-known expression [12].

The composition dependence of microhardness (H) is given in Fig. 3. It is seen that for the $AgInS_2$–$CuInS_2$ system Kurnakov's rule is valid. According to this, for the formation of the complete series of solid solutions in the system the composition dependence of H is expressed by a smooth curve having a maximum [13, 14]. This maximum for the $Ag_xCu_{1-x}InS_2$ solid solutions corresponds to the composition with $x = 0.2$. Using the expression proposed by us [15] the calculation of H was made. These values are denoted by solid lines. It is seen that the calculated values and experimental ones agree very well. The calculated position of the maximum corresponds to $x = 0.17$ and also agrees very well with the experimental one (0.2). These results reaffirm the formation of the complete series of solid solutions in the $AgInS_2$–$CuInS_2$ system.

3.4. Transmission spectra

The transmission spectra of the $Ag_xCu_{1-x}InS_2$ solid solutions in the range of the fundamental absorption were taken using SP-700C and Beckman 5270 spectrophotometers. The investigations were carried out for the polarized radiation at 77 and 293 K. Crystals were mechanically lapped and polished from two sides to a thickness d of about 20 µm. The absorption

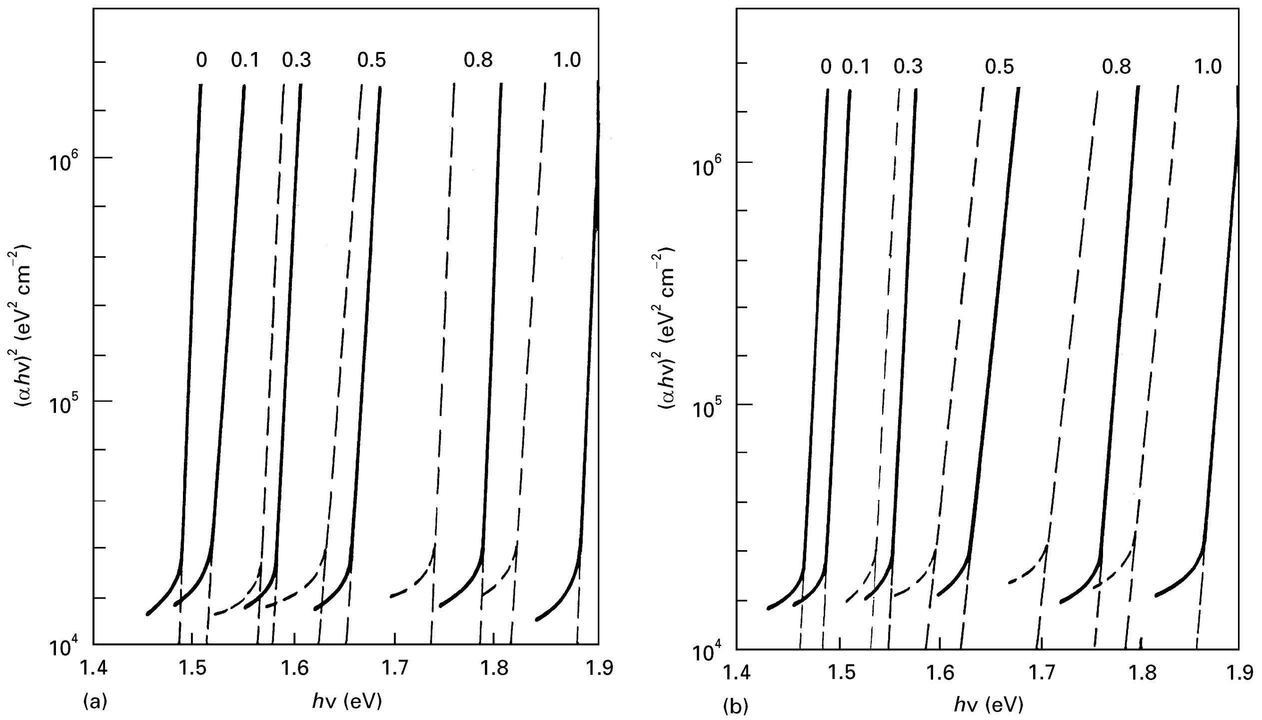

Figure 4 The spectral dependencies of $(\alpha h\nu)^2$ at 77 K (a) and 293 K (b) for the $Ag_xCu_{1-x}InS_2$ solid solutions for the $E \perp c$ (solid curves) and $E \parallel c$ (broken curves) direction of polarization.

coefficient α was calculated using the well-known expression

$$\alpha = \frac{1}{d}\ln\left\{\frac{(1-R)^2}{2T} + \left[\frac{(1-R)^4}{4T^2} + R^2\right]^{1/2}\right\} \quad (1)$$

where R is the reflectivity coefficient and T is the transmission coefficient. As the I–III–VI_2 ternary chalcopyrite compounds are the direct gap semiconductors that the band gap E_g was estimated by extrapolation of the linear part of $(\alpha h\nu)^2$ versus photon energy to the intersection with the photon energy axis. Fig. 4 gives the spectral dependencies of $(\alpha h\nu)^2$ for the $AgInS_2$ and $CuInS_2$ compounds and their solid solutions at 77 and 293 K. These dependencies have clear expressed linear parts that tells us about the homogenization of grown crystals. The estimated values of E_g with the error of estimation 0.005 eV for $AgInS_2$ are 1.877 and 1.815 eV at 77 K, 1.855 and 1.782 eV at 293 K for $E \perp c$ and $E \parallel c$, respectively. The transmission spectra of $CuInS_2$ are not sensitive to polarization of radiation. It may be connected with the absence of distortion of tetragonal lattice of this compound. The second reason for this may be the fact that because of using (1 1 2) plane of single crystal the $E \parallel c$ polarization is not complete [16]. The values of E_g for $CuInS_2$ are 1.482 eV at 77 K and 1.460 eV at 293 K. The transmission spectra for the solid solutions with the ratio $c/a = 2.015 \ldots 2.008$ do not also depend on the direction of polarization.

The composition dependence of E_g for the $Ag_xCu_{1-x}InS_2$ solid solutions is given in Fig. 5. Its change with composition has non-linear behaviour that is typical for the solid solutions based on the I–III–VI_2 compounds when the cation substitution takes place. To explain the non-linear behaviour of this dependence there are two approaches at this time. They are the dielectric model and pseudopotential model [17–19]. The composition dependence of E_g for the I-III-VI_2-based solid solutions approximately can be expressed by the following equation

$$E_g(x) = E_g^{(0)} + (E_g^{(1)} - E_g^{(0)} - c)x + cx^2 \quad (2)$$

where $E_g^{(0)}$ and $E_g^{(1)}$ are the band gap of the initial compounds with the lower and higher value of the band gap respectively (in this case $E_g^{(0)}$ is attributed to $CuInS_2$ and $E_g^{(1)}$ is attributed to $AgInS_2$), c is the bowing parameter. This parameter is calculated using the following expression

$$c = 4[0.5(E_g^{(0)} + E_g^{(1)}) - E_g^{(0.5)}] \quad (3)$$

where $E_g^{(0.5)}$ is the band gap for the solid solution with $x = 0.5$.

The composition dependencies of E_g at 77 K for the $Ag_xCu_{1-x}InS_2$ solid solutions can be analytically expressed by the following equations

$$E_g(x) = 1.482 + 0.277x + 0.118x^2 \quad (4)$$

for $E \perp c$ and

$$E_g(x) = 1.482 + 0.239x + 0.094x^2 \quad (5)$$

for $E \parallel c$. The analogous equations for the temperature of 293 K are

$$E_g(x) = 1.460 + 0.245x + 0.150x^2 \quad (6)$$

for $E \perp c$ and

$$E_g(x) = 1.460 + 0.178x + 0.144x^2 \quad (7)$$

for $E \parallel c$.

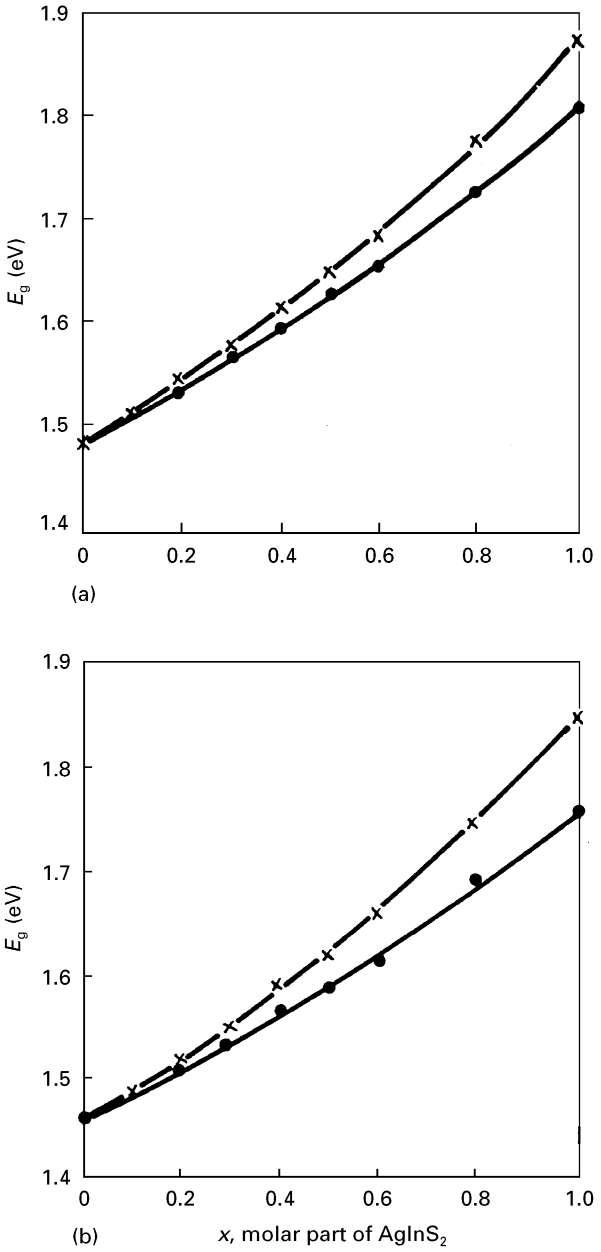

Figure 5 The composition dependence of E_g for the $Ag_xCu_{1-x}InS_2$ solid solutions at 77 (a) and 293 K (b) for the $E \perp c$(x) and $E \parallel c$ (o) direction of polarization.

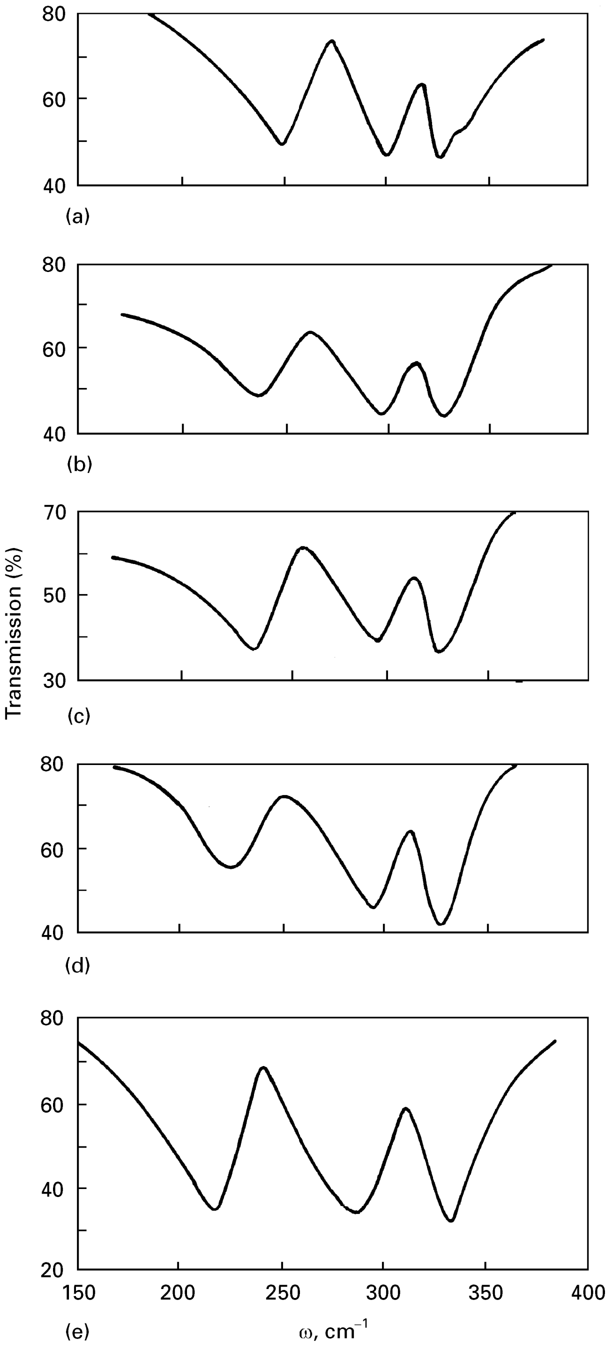

Figure 6 The infrared transmission spectra of the $Ag_xCu_{1-x}InS_2$ solid solutions. (a) $x = 0$; (b) $x = 0.3$; (c) $x = 0.5$; (d) $x = 0.7$; (e) $x = 1$.

3.5. Infrared transmission spectra

The infrared transmission spectra of the $Ag_xCu_{1-x}InS_2$ solid solutions were investigated in the range from 150 to 400 cm^{-1}. For this purpose the obtained crystals were crushed and powdered. This powder and hot polyethylene in mass ratio 1 : 50 were used to press tablet. Fig. 6 gives the infrared transmission spectra for the $AgInS_2$, $CuInS_2$ compounds and their solid solutions. It is seen the $CuInS_2$ compound has four absorption bands with maximums at 248, 300, 325 and 335 cm^{-1}. $AgInS_2$ displays three absorption bands (220, 289 and 330 cm^{-1}). The band with maximum at 335 cm^{-1} is displayed for the solid solutions with x in the range from 0 to 0.1. With the increasing of content of argentum the frequencies of optical phonons are shifted to the low frequency range (Fig. 7), the intensities of these bands are not changed. The low frequency bands with maxima at 220–248 cm^{-1} are the most sensitive to this substitution. These bands correspond to the vibrations of the Cu(Ag)–S bond. The high frequency bands which correspond to the vibrations of the In–S bond are less sensitive to the substitution of copper by argentum. It says that the $Ag_xCu_{1-x}InS_2$ solid solutions in the investigated range show single mode behaviour.

4. Conclusions

The phase equilibriums of the $AgInS_2$–$CuInS_2$ system were investigated by means of X-ray diffraction and differential thermal analysis and the T–x phase diagram of this system was constructed. This diagram has a complex look with many solid state transitions (from

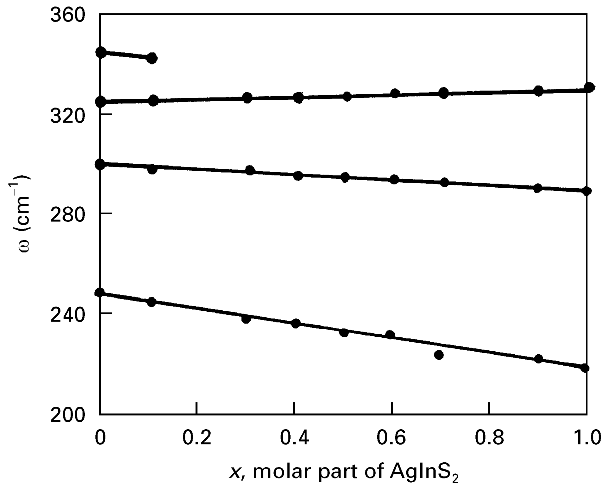

Figure 7 The composition dependence of the frequencies of optical phonons for the $Ag_xCu_{1-x}InS_2$ solid solutions.

chalcopyrite to rhombic structure, from chalcopyrite to sphalerite structure, and presumably from sphalerite to wurtzite structure). The formation of solid solutions for the complete range of compositions was discovered. The large grain crystals of the $Ag_xCu_{1-x}InS_2$ solid solutions in the complete range of compositions were grown by the two-zone method with following directed crystallization of melt. The composition dependencies of microhardness, transmission spectra in the range of the fundamental absorption, infrared transmission spectra in the range from 150 to 400 cm^{-1} for the $Ag_xCu_{1-x}InS_2$ solid solutions were investigated. It was discovered that the composition dependence of microhardness is expressed by smooth curve having maximum for $x = 0.2$. The composition dependence of band gap has non-linear behaviour that is typical for the solid solutions based on the I–III–VI_2 compounds with the cation substitution. These dependencies have been analytically expressed at 77 and 293 K for the $E \perp c$ and $E \parallel c$ direction of polarization. From the studies of the infrared transmission spectra the frequencies of optical phonons were determined and it was discovered that their composition dependence shows single mode behaviour.

Acknowledgements

The authors are grateful to the Ministry of Science and Education of the Republic of Belarus for financial support of these studies.

References

1. H. HAHN, G. FRANK, W. KLINGLER, A. D. MEYER and G. STORGER, *Z. Anorg. Allg. Chem.* **271** (1953) 153.
2. K. CHOPRA and S. DASS, in "Thin films solar cells" (Chapman and Hall, London, 1983) p. 440.
3. Y. V. RUD and Z. A. PARIMBEKOV, *Fiz. Tekh. Poluprov.* **17** (1983) 281.
4. Y. V. RUD, *Zhurn. Tekh. Fiz.* **54** (1984) 2253.
5. M. ROBBINS, J. C. PHILIPS and V. C. LAMBRECHT, *J. Phys. Chem. Solids* **34** (1973) 1205.
6. G. SHARLO, in "Methods of analytical chemistry" (Chimia Press, Moscow, 1965) p. 712.
7. N. N. ISCHENKO, L. G. STAROBINETS and L. I. GANAGO, *Izv. AN BSSR. Ser. Chim. Nauk* **5** (1977) 132.
8. L. G. STAROBINETS, N. N. ISCHENKO and L. I. GANAGO, *Izv. AN BSSR Ser. Chim. Nauk.* **1** (1988) 111.
9. T. P. TSVETKOVA, T. P. SAHAROVA and Z. S. BESKOVA, *Elektr. Tekh. Ser. Mater.* **7** (1976) 124.
10. L. S. PALATNIK, V. M. KOSHKIN and L. P. GALCHINETSKII, *Fiz. Tv. Tela* **4** (1962) 2365.
11. I. V. BODNAR, *Izv. AN SSSR Ser. Neorg. Mater.* **17** (1981) 583.
12. V. M. GLAZOV and V. N. VIGDOROVICH, in "Microhardness of metals and semiconductors" (Metallurgia Press, Moscow, 1969) p. 248.
13. N. S. KURNAKOV, in "Selected papers" (Press of Academy of Sciences of USSR, Moscow, 1960) p. 596.
14. N. S. KURNAKOV, in "Introduction to physico-chemical analysis" (Press of Academy of Sciences of USSR, 1940) p. 562.
15. I. V. BODNAR, B. V. KORZOUN and A. P. CHERNYAKOVA, *Phys. Status Solidi* (*a*) **101** (1987) 409.
16. N. YAMAMOTO and T. MIYAUCHI, *Bull. Univ. Osaka Prefect.* **A 23** (1974) 147.
17. D. JONES and A. H. LETTINGTON, *Solid State Commun.* **7** (1969) 1319.
18. R. HILL and D. RICHARDSON, *J. Phys. C* **6** (1973) L115.
19. R. HILL, *ibid.* **7** (1974) 521.

Received 14 June 1996
and accepted 24 July 1997