

Growth and characterization of some I–III–VI₂ compound semiconductors

K. BALAKRISHNAN, B. VENGATESAN, P. RAMASAMY
Crystal Growth Centre, Anna University, Madras 600 025, India

Single crystals of CuInS₂, CuInSe₂, CuInTe₂, CuGaS₂, AgGaS₂, CuInSSe, AgGaSSe have been grown by chemical vapour transport technique on the basis of a new general thermodynamical model which enables the minimum source temperature T_s , and the minimum deposition temperature, T_d , to be determined. X-ray analysis, X-ray photoelectron spectroscopic analysis, surface analysis, and microhardness studies have been carried out on the single crystals grown.

1. Introduction

Ternary and pseudo-ternary A^IB^{III}C^{VI} compounds are attracting attention from a fundamental point of view as a third generation of semiconducting materials after elemental and binary systems. These ternary and pseudo-ternary compounds are interesting for their possible applications in tuning lattice parameters and optical gaps [1] in order to obtain compounds tailored to meet specific photoconductive and non-linear optical demands. High-efficiency solar cells are often fabricated using single crystals of CuInS₂ and CuInSe₂ [2, 3]. In the present investigation, a general thermodynamic model to fix the minimum source temperature, T_s , and the minimum deposition temperature, T_d , for the efficient transport of ternary chalcopyrite compounds has been proposed. The proposed model has been verified experimentally with CuInS₂ and CuInSe₂. Single crystals of some ternary chalcopyrite compounds, such as CuInS₂, CuInSe₂, CuInTe₂, CuGaS₂, AgGaS₂ and pseudo-ternary compounds, namely CuInSSe and AgGaSSe, have been grown by chemical vapour transport (CVT) using iodine as the transporting agent, and characterization studies, such as X-ray analysis, X-ray photoelectron spectroscopic (XPS) analysis, microscopic analysis and microhardness studies have been carried out for the single crystals grown.

2. Thermodynamic model

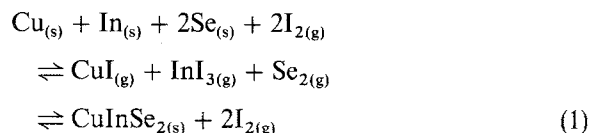
In the present work, an attempt has been made to consider thermodynamic analysis of the chemical vapour transport of ternary chalcopyrites by taking the elements as the source materials. Prediction of the minimum source temperature, T_s , and the minimum growth temperature, T_d , for the growth of ternary chalcopyrite compounds (CuInS₂, and CuInSe₂) have been made on the basis of this proposed model. The model has been extended to predict the experimental conditions for the growth of CuInS₂ and CuInSe₂ with hydrogen iodide as the transporting agent. Further, this model can be used to study the minimum

source temperature and growth temperature for other chalcopyrite compounds.

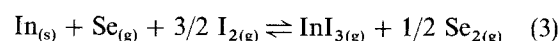
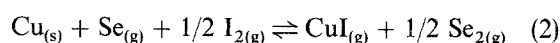
The components in stoichiometric proportions are converted into gaseous binary compounds by the reaction of the transporting agent. It is obvious that the gas phase during chemical transport of a ternary compound contains the same species as during hypothetical simultaneous transport of the components. The conditions under which deposition of the ternary compound will occur can be predicted if the ΔG function of all possible solid to gas equilibrium reactions in the transport systems are known. A feasibility study of the transport of a ternary compound, therefore, reduces to the evaluation of the ΔG functions of such reactions.

2.1. Application of the proposed model to CuInSe₂

When the constituent elements, namely, copper, indium, selenium in the case of CuInSe₂, are taken in stoichiometric ratio together with the transporting agent iodine at the source end, they react to form the gaseous binary iodides and selenium at high temperature. All these gaseous species diffuse to the colder growth zone due to the drop in temperature. At the growth zone they react back to form the ternary chalcogenide with the release of iodine. The iodine liberated diffuses back to the source end to form the metal iodides once again.



As stated above, the gas phase during a chemical vapour transport reaction contains the same species as during a hypothetical transport of the constituent elements occurring simultaneously. The hypothetical transport reactions of the elements are as follows



In general, ΔG is given by the equation

$$\Delta G = \Delta G^\circ + RT \ln K_p \quad (4)$$

where ΔG° is the standard free energy change, R the gas constant, T the temperature, and K the equilibrium constant. The source temperature is determined upon predicting the conditions under which CuI and InI_3 form (i.e. conditions under which the free energy change corresponding to the Equations 2 and 3 become negative). In the same way, the source temperature of CuInSe_2 with HI and CuInS_2 with I_2 and HI as the transporting agents and deposition temperatures have been predicted (Table I). The dependence of ΔG on temperature for a fixed iodine (transporting agent) concentration is represented in Fig. 1.

3. Experimental procedure

For the growth of crystalline ABC_2 , high-purity elements A (Cu, Ag), B (In, Ga), C (S, Se, and S and Se in the case CuInSSe and AgGaSSe) in stoichiometric

TABLE I Predicted values of minimum source and deposition temperatures

Compound	Source	Transport agent	Predicted minimum T_s (K)	Predicted minimum T_d (K)
CuInSe_2	Cu:In:Se	I_2	901	835
CuInSe_2	Cu:In:Se	HI	1250	1100
CuInS_2	Cu:In:S	I_2	1025	844
CuInS_2	Cu:In:S	HI	1640	1480

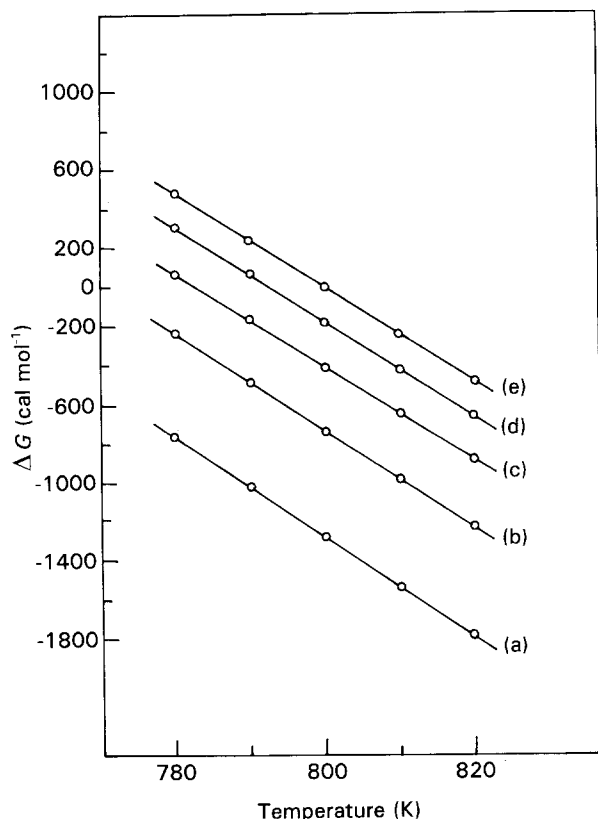
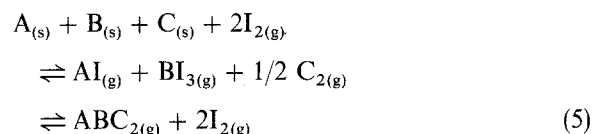


Figure 1 The variation of ΔG with temperature for different iodine concentrations (CuInSe_2): (a) 1 mg cm^{-3} , (b) 2 mg cm^{-3} , (c) 3 mg cm^{-3} , (d) 4 mg cm^{-3} , (e) 5 mg cm^{-3} .

ratio and trace amounts of iodine have been taken in a quartz ampoule of 200 mm length and 10 mm diameter with a narrow extension to suppress the spurious nucleation. The ampoule was evacuated to a vacuum of 10^{-6} torr and then placed in a horizontal kanthal coiled double zone furnace and the zone temperatures were maintained steady, correct to $\pm 1^\circ\text{C}$ by means of thyristorized controllers. The growth zone was cleaned, initially maintaining the temperature higher than the source zone for 24 h. After this the temperature gradient was reversed and the source temperature and deposition temperature were kept constant at two different values.

4. Results and discussion

Crystals of ABC_2 were deposited at the colder tip of the ampoule after about 100 h. The formation of ABC_2 may be due to the chemical reaction



In this way, single crystals of CuInS_2 , CuInSe_2 , CuInTe_2 , CuGaS_2 , CuInSSe , AgGaS_2 and AgGaSSe have been grown with different transporting agent concentrations. Table II gives the growth details of the single crystals grown. Figs 2–6 show the single crystals of CuInS_2 , CuInSe_2 , CuInSSe , CuInTe_2 and CuGaS_2 , respectively.

TABLE II Growth details of the single crystals grown

Crystal	Source temperature T_g ($^\circ\text{C}$)	Growth temperature T_d ($^\circ\text{C}$)	Transporting agent	Size (mm^3)
CuInS_2	830	800	I_2	$7 \times 3 \times 1$
CuInSe_2	810	770	I_2	$5 \times 3 \times 2$
CuInTe_2	710	670	$\text{I}_2 + \text{TeCl}_4$	$3 \times 1 \times 1$
CuGaS_2	840	750	I_2	$3 \times 1 \times 1$
AgGaS_2	930	890	I_2	$3 \times 2 \times 1$
CuInSSe	950	900	I_2	$3 \times 2 \times 1$
AgGaSSe	935	855	I_2	$4 \times 2 \times 2$

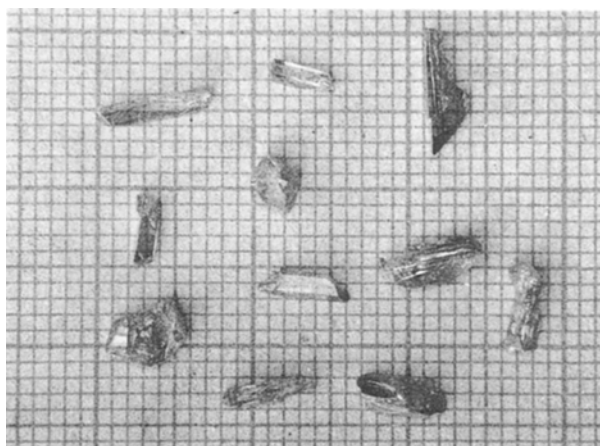


Figure 2 Crystals of CuInS_2 .

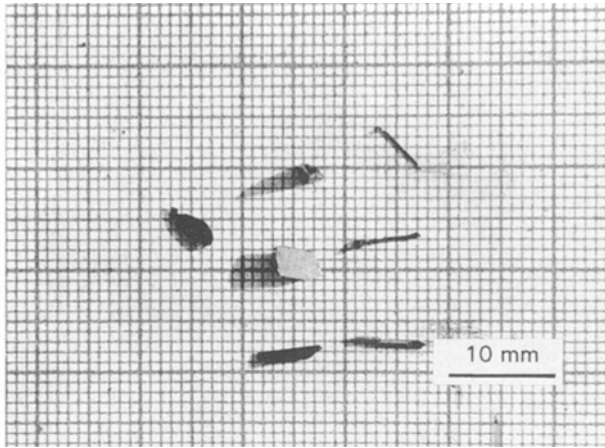


Figure 3 Crystals of CuInSe_2 .

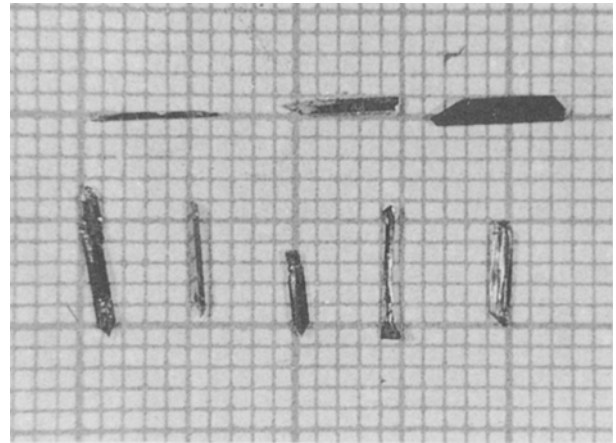


Figure 6 Crystals of CuGaS_2 .

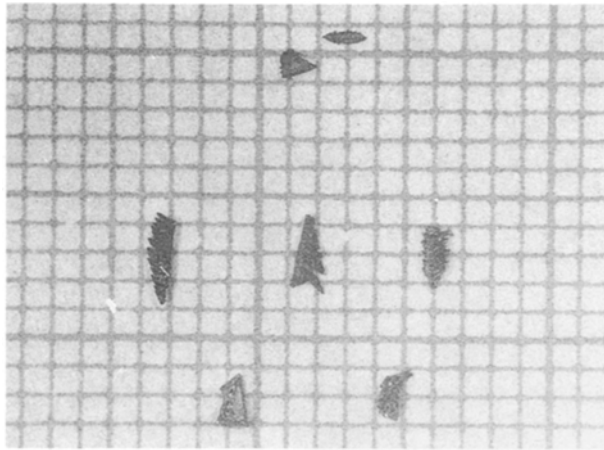


Figure 4 Crystals of CuInSSe .

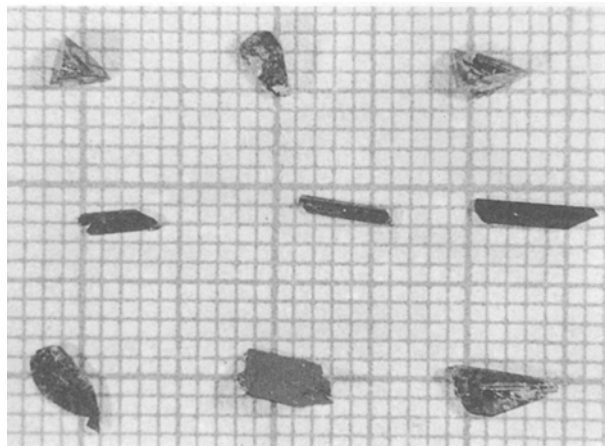


Figure 5 Crystals of CuInTe_2 .

TABLE III Lattice parameters of the crystals

Crystal	a (nm)	c (nm)	Reference
CuInS_2	0.551	1.105	[4]
CuInSe_2	0.578	1.162	[5]
CuInSSe	0.543	1.127	Present work
CuInTe_2	0.616	1.232	[6]
CuGaS_2	0.535	1.048	[6]
AgGaS_2	0.574	1.027	[6]
AgGaSSe	0.571	1.046	Present work

4.1. X-ray and XPS analyses

The crystalline behaviour of the grown crystals was investigated by taking X-ray powder diffractograms using CuK_α radiation. For CuInS_2 , CuInSe_2 , CuInTe_2 , CuGaS_2 and AgGaS_2 crystals lattice parameter have been found and verified with the literature. Because there is no ASTM report for CuInSSe and AgGaSSe compounds, crystallographic data had to be established. The system of the compounds was found to be tetragonal, which implies that CuInSSe and AgGaSSe crystallize in the same manner as their parent compounds CuInS_2 and CuInSe_2 , and AgGaS_2 and AgGaSe_2 , respectively. The lattice parameter of the crystals are tabulated in Table III.

XPS analysis was carried out for the crystals and the presence of all the elements was confirmed. It was also confirmed from the XPS analysis that the crystals grown contain no impurities and the stoichiometry was confirmed with the help of chemical analysis. Fig. 7 shows the XPS recording of the CuInSSe crystal.

4.2. Microscopic analysis

In order to study the microstructural details of the crystals grown, scanning electron microscopy (SEM) and optical microscopy with high resolution were employed. Gold coating was made on all the samples before they were analysed by SEM. Fig. 8 shows the microcrystals observed on the surfaces of CuInSSe crystals. This kind of microcrystal was observed to adhere over the $[001]$ faces. They have random orientations and there were no crystallographic orientation between these crystals and the host crystal. The presence of one or more nuclei in a supersaturated vapour often leads to multicrystallization which otherwise could not occur. This is called secondary nucleation [7], which is referred to that arising from faceted crystals, rather than arm detachment from dendrites. This kind of microcrystal was not observed in the inner surfaces of the crystals (i.e. on the cleaved surfaces). So it may be said that they must have formed only during the termination of the growth run.

The round-bottomed hillocks have been observed on several faces of the CuInSe_2 crystals. Fig. 9 shows

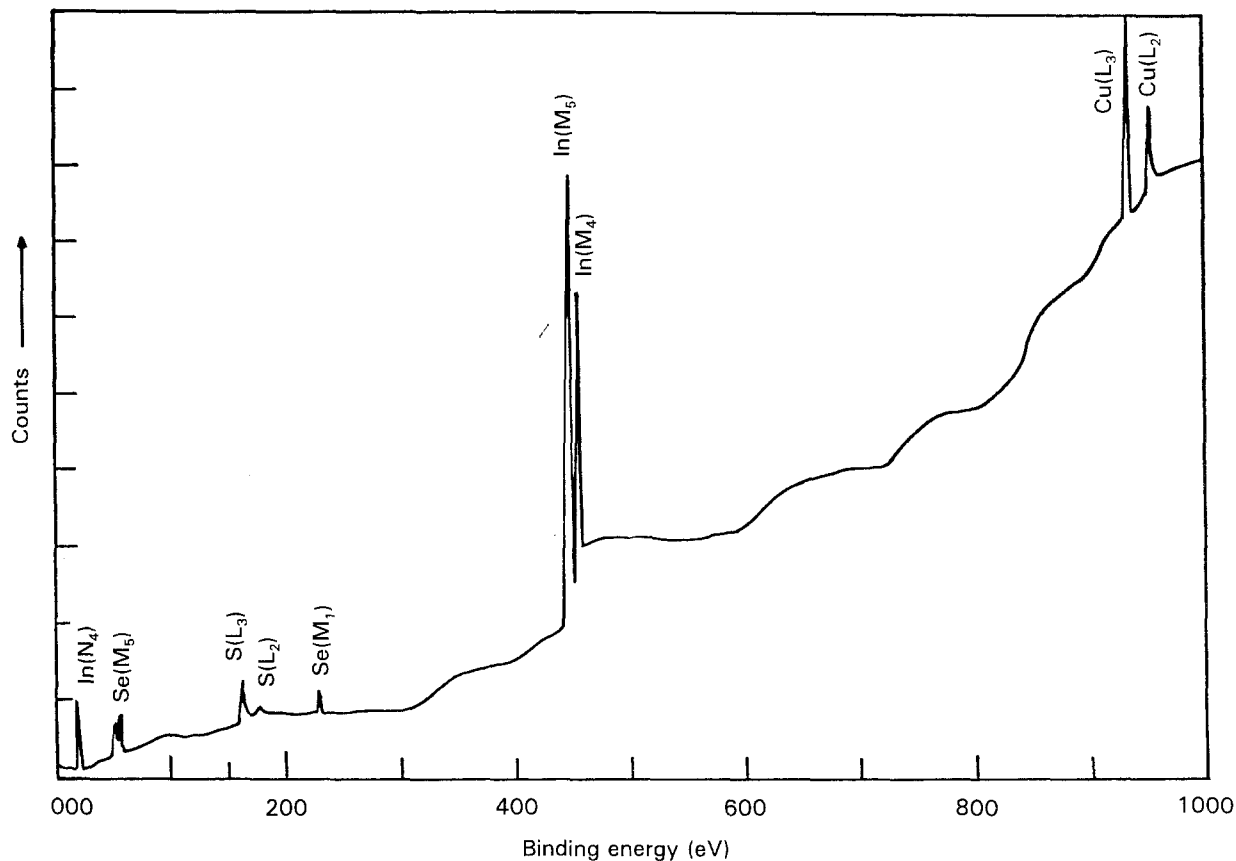


Figure 7 XPS spectrum of CuInSSe.

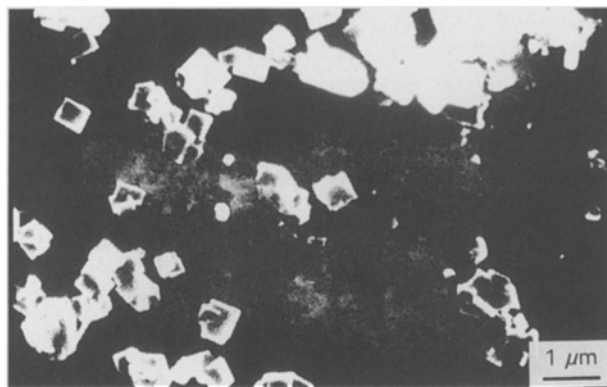


Figure 8 Microcrystals of CuInSSe.

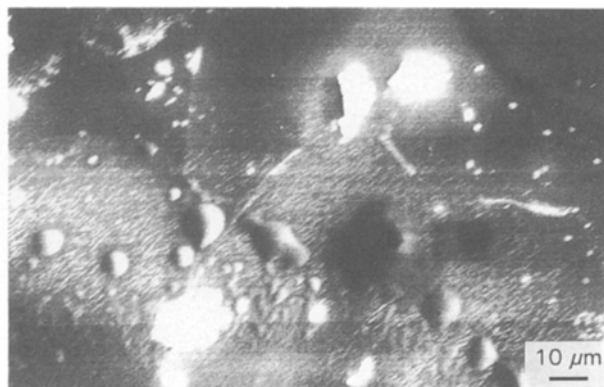


Figure 9 Growth hillocks observed on CuInSe₂ crystals.

the typical round-bottom hillocks. These hillocks are tapered sharply and the diameter is about 20 μm. The occurrence of round-bottomed hillocks may be due to the relatively slow growth rate. Crystals exhibiting non-polygonized hillocks are considered to be better quality crystals. There are two types of hillocks, polygonized and non-polygonized or round hillocks [8]. Sunagawa [9] discussed the formation of the hillocks and suggested that they might be due to the spiral mechanism with short intervals grown around the imperfections. Microsteps have been observed on the hillocks by Roberts and Elwell [10, 11]. These hillocks are named active growth centres.

Figs 10 and 11 show the spiral growth which occurred in the case of CuInS₂ crystals. The presence of these steps allows the crystals to grow continuously

without the nucleation process. It is speculated that the growth might be due to the layer growth mechanism at the edges and propagating towards the centre. The presence of impurity atoms might be the reason for the propagation of the spirals [12].

4.3. Microhardness studies

Hardness is an important solid-state property: hardness tests are commonly carried out to determine the mechanical strength of materials, and the value correlates with mechanical properties such as elastic constants and yield strength. As hardness properties are basically related to the crystal structure of the material, microhardness studies have been applied in order to understand the plasticity of the crystals [13].

TABLE IV Mechanical properties of the crystals

Crystal	Hardness H_v (kg mm^{-2})	Work-hardening coefficient	Fracture toughness ($\text{MPa m}^{1/2}$)	Brittleness index ($\mu\text{m}^{-1/2}$)	Yield strength (GPa)
CuInS_2	293	1.71	0.764	3.91	0.976
CuInSe_2	270	1.60	0.702	3.84	0.883
CuInTe_2	208	1.42	0.643	3.43	0.807
CuInSSe	279	1.64	—	—	—
AgGaS_2	461	2.58	—	—	—

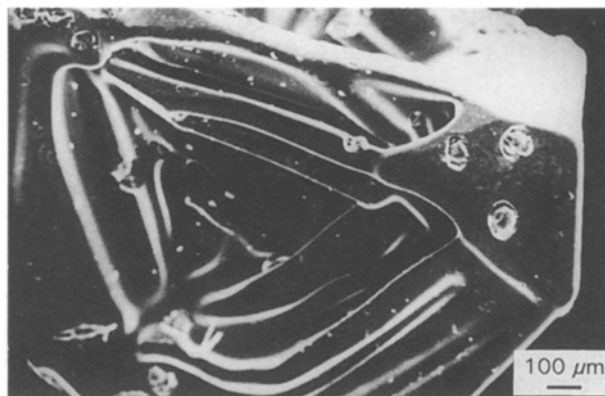


Figure 10 Spiral pattern observed in CuInS_2 .

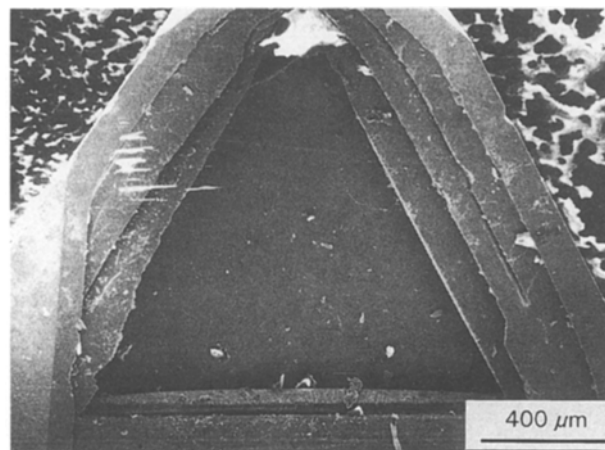


Figure 11 Step growth observed in CuInS_2 .

Microhardness studies on selected smooth surfaces of the grown crystals were carried out by subjecting them to static indentation tests in air at room temperature (300 K) using a Leitz Wetzlar hardness tester fitted with a Vickers pyramidal indenter and attached to a Leitz incident light microscope. The load, p , was varied from 2–100 g. Keeping the indentation time constant at 10 s, for each crystal several trials of indentation with each load were carried out and the average value of the diagonal length of the indentation marks in each trial was calculated. This value was used to estimate the microhardness at the applied load using the equation [14]

$$H_v = 1.85 P/d^2 \text{ kg mm}^{-2} \quad (6)$$

Table IV gives the calculated Vickers microhardness values and some mechanical properties for the crystals grown.

9. Conclusion

The proposed general thermodynamic model enables the minimum source temperature and the minimum deposition temperature for the effective transport of ternary compounds to be determined. Single crystals of CuInS_2 , CuInSe_2 , CuInSSe , CuInTe_2 , CuGaS_2 , AgGaS_2 , AgGaSSe have been grown by the chemical vapour transport technique using iodine as the transporting agent, and characterization studies such as X-ray analysis, XPS analysis, surface analysis and microindentation studies have been carried out on the grown crystals.

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