

Review

THM Growth of Ternary and Multinary Chalcopyrite Semiconductors

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Abstract

The traveling heater method (THM), which is one of the solution growth techniques, has been applied to the single crystal growth of the I-III-VI₂ chalcopyrite semiconductors. It is generally difficult to grow high-quality single crystals of the I-III-VI₂ compounds from the stoichiometric melts, because most of the compounds grow through a peritectic reaction or a solid state transition during the cooling process. Up to this time, bulk single crystals of CuGaS₂, CuGaSe₂, CuGaTe₂, CuInS₂, CuInSe₂ and CuInTe₂ ternary compounds have been obtained by the THM technique using In solvent. Bulk single crystals of CuGa_xIn_{1-x}S₂ and CuGa_xIn_{1-x}Se₂ quaternary alloys have also been grown by the THM with In-solution zones, in which the compositions were adjusted to obtain homogenous crystals having intended compositions *x*. Furthermore, THM growth of AgGaS₂ and CuGaS₂ single crystals has been performed by using PbCl₂ and CuI halide solvents, respectively.

Key words : Chalcopyrite semiconductors, I-III-VI₂ compounds, Single crystal growth, Traveling heater method (THM), Solution growth, Copper indium diselenide

1. Introduction

The I-III-VI₂ compounds with a chalcopyrite structure have received much attention in recent years. Fig. 1 shows band-gap energies and lattice constants of the Cu-III-VI₂ and Ag-III-VI₂ compounds[1]. The compounds with relatively large band gaps are expected to have applications for optoelectronic devices in the short-wavelength region [2-18], and the Cu-III-VI₂ compounds with band gaps of 1.0~1.7 eV have attracted considerable interest because of possible photovoltaic applications [19-26]. The thin-film solar cells with a CuGa_xIn_{1-x}Se₂ absorber have achieved conversion efficiencies exceeding 17% [27,28]. In addition, the AgGaS₂ and AgGaSe₂ crystals are already used for nonlinear optical devices [29-31].

CuAlS₂ and CuAlSe₂ have dominantly p-type electrical conductivity and the II-VI compounds ZnS and ZnSe show normally n-type conduction, and the latter compounds are fairly well lattice-matched to the former ones, respectively. Hence, the heterojunctions between the p-type I-III-VI₂ and n-type II-VI compounds have promise of high-quality blue-light-emitting devices. ZnS or ZnSe epilayers can be grown at low temperatures below 300 °C [32,33], but relatively high temperatures are needed for epitaxy of I-III-VI₂ compounds [3-15]. Hence, epitaxy of the II-VI compounds on the I-III-VI₂ compounds is desirable rather than that of I-III-VI₂ on II-VI for fabrication of the heterojunctions. Since growth of bulk single crystals of CuAlS₂ and CuAlSe₂ is difficult because Al is chemically active, they have been grown epitaxially on substrates of II-VI and III-V compounds [10-12]. But, interdiffusion of between the epilayer and the substrate has induced unfavorable change in their properties. The ternary compounds CuGaS₂ and CuGaSe₂ belonging to the same I-III-VI₂ family will be preferable as alternative substrates, in order to reduce the effect of interdiffusion between the epilayer and the substrate. Therefore, bulk single crystals of CuGaS₂ and CuGaSe₂ are required for the epitaxy of CuAlS₂ and CuAlSe₂, respectively [34,35].

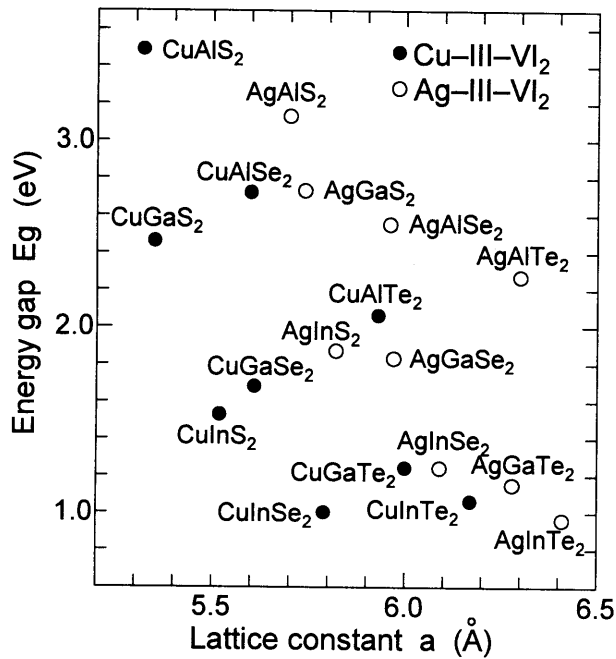


Fig.1 Energy gaps and lattice constants of I-III-VI₂ ternary compounds

I-III-VI₂ compounds having relatively narrow band gaps, CuInS₂, CuInSe₂ and CuGaSe₂ ternary compounds and CuGa_{1-x}In_xSe₂ [36] and CuIn(S_xSe_{1-x})₂ [37] quaternary alloys, are promising as materials for heterojunction solar cells with Cd(Zn)S and/or ZnO window layers. CuGaTe₂ and CuInTe₂ are also expected as the alternative absorbers of the photovoltaic devices. Although most of studies on these compounds have been concerned with polycrystalline thin films, studies on properties of the bulk single crystals will be helpful for improvement of the solar cells.

AgGaS₂ and AgGaSe₂ have unique nonlinear infrared optical properties, and can be phase matched through relatively wide portions of their transparency ranges. AgGaS₂ is transparent from 0.45 to 13 μm and phase matched for second-harmonic generation (SHG) for fundamental wavelengths from 1.8 to 11 μm [38]. AgGaSe₂ is transparent from 0.73 to 17 μm and phase matched for SHG for fundamental wavelengths from 3.1 to 13 μm [39].

Single crystals of I-III-VI₂ compounds have been grown by a variety of techniques from vapor, melt and solution. The vapor phase growth, which is typically iodine chemical vapor transport technique, yields single crystals of rather high quality, but the grown crystals are small and irregular in shape. For fabrication of the devices and detailed examination of the optical and electrical properties, it is necessary to use large bulk single crystals. Table 1 shows studies of the growth from melt and solution in order to obtain large bulk I-III-VI₂ single crystals. In this review, we describe the single crystal growth of I-III-VI₂ ternary and quaternary compounds by THM.

2. Phase diagram and melt growth of I-III-VI₂ compounds

For preparation of bulk crystals, information about the phase diagrams is indispensable. Phase diagrams for I-III-VI₂ chalcopyrite compounds have usually been investigated along the I₂VI-III₂VI₂ pseudobinary lines [66-74]. The growth mechanisms of chalcopyrite crystals from stoichiometric melts and the temperatures of the phase transition related to the growth are summarized in Table 1. While AgGaS₂ and AgGaSe₂ crystals with chalcopyrite structure are directly grown by cooling from their stoichiometric melts [41], the compositions of the obtained crystals deviate from stoichiometry owing to incongruent melting. Most of Cu-based chalcopyrite compounds (Cu-III-VI₂) are produced from the melts through a peritectic reaction or a solid state transition during cooling process. For the Cu-Ga-Se system, a peritectic point exists at a temperature (T_p=1030 °C) below the melting point of the stoichiometric CuGaSe₂ [67], and for the Cu-Ga-Te, Cu-In-S, Cu-In-Se and Cu-In-Te systems, the chalcopyrite crystals are grown through a solid-state phase transition from the zincblende-type crystals, as summarized in Table 1. The detailed phase diagram of Cu-Ga-S system is not known, but crystals grown from the stoichiometric CuGaS₂ melts have off-stoichiometric compositions and considerably high temperature is required for the growth [66,75]. In order to obtain bulk single crystals without the adverse effects associated with the melt growth, the solution growth technique is preferable, since the growth can be performed at temperatures below the transition points.

Table 1. Growth of the bulk I-III-VI₂ single crystals

| Compound | Melting point(°C) | Growth mechanism of chalcopyrite from stoichiometric melt | Transition temp.(°C) | Single crystal | growth | |
|--|----------------------|---|-------------------------|-------------------|--------------------|---------|
| | | | | Technique* | Solvent | Ref. |
| AgGaS ₂ | 1040 | direct(incongruent) | | BM | ----- | [40,41] |
| | | | | LEC | ----- | [42] |
| | | | | THM | PbCl ₂ | [43] |
| AgGaSe ₂ | 850 | direct(incongruent) | | BM | ----- | [41] |
| AgGaTe ₂ | 720 | eutectic reaction | 680 | BM | ----- | [44,45] |
| CuGaS ₂ | 1250 | incongruent | | THM | In | [46] |
| | | | | THM | CuI | [47] |
| CuGaSe ₂ | 1090 | peritectic reaction | 1030 | THM(ZM) | Cu ₂ Se | [48] |
| | | | | THM | In | [49] |
| | | | | THM | Ga | [50] |
| | | | | TSSG | In | [51] |
| CuGaTe ₂ | 862 | phase trans. in solid | 720 | BM | ----- | [52] |
| | | | | THM | In | [53] |
| CuInS ₂ | 1050 | phase trans. in solid | 980 | GF | ----- | [54,55] |
| | | | | THM | In | [56] |
| CuInSe ₂ | 986 | phase trans. in solid | 810 | BM | ----- | [23,24] |
| | | | | ZM | ----- | [23,57] |
| | | | | LEC | ----- | [58] |
| | | | | GF(NF) | ----- | [22] |
| | | | | THM | In | [59,60] |
| CuInTe ₂ | 789 | phase trans. in solid | 672 | BM | ----- | [61] |
| | | | | ZM | ----- | [62] |
| | | | | GF | ----- | [63] |
| | | | | THM | In | [64] |
| CuGa _{0.6} In _{0.4} S ₂ | | | | THM | In | [65] |
| CuGa _x In _{1-x} Se ₂ | | phase trans. in solid | | THM | In | [36] |

*BM: Bridgman(-Stockbarger) method, LEC: liquid encapsulated Czochralski method

THM: traveling heater method, ZM: zone melting method, TSSG: top-seeded solution growth method

GF: gradient freezing method, NF: normal freezing method

Melt growth technique has been attempted for many I-III-VI₂ ternary compounds, as shown in Table 1. AgGaS₂ and AgGaSe₂ crystals are grown by means of Bridgman method by Feigelson and Route, and the crystals with 37 mm in diameter and several centimeter in length were obtained [41]. However, owing to incongruent melting, the obtained AgGaS₂ and AgGaSe₂ crystals are always a few percent richer in Ga₂S₃ and Ga₂Se₃ than the stoichiometric compositions, respectively, so that microscopic scattering defects are inevitably included. In order to remove the defects, postgrowth heat treatment with Ag₂S or Ag₂Se must be performed for 10 to 15 days at temperatures near the melting points.

CuInSe₂ single crystals have been obtained by using various melt growth techniques, such as Bridgman (-Stockbarger) [23,24], gradient freezing and normal freezing methods [22]. For the growth from the melt, the crystals with chalcopyrite structure are formed through a solid-state phase transition from the zincblende-type crystals during the cooling process, as described in the previous section. Hence, the growth must be performed with low cooling rates, typically 1~2°C/h, down to the temperatures below 810°C [68].

LEC (liquid encapsulated Czochralski) technique is used for growth of large bulk single crystals of many compound semiconductors. To our knowledge, there are two reports of LEC growth of I-III-VI₂ compounds. The first experiment was for AgGaS₂ [42], and the other one was for CuInSe₂ [58]. The LEC-grown AgGaS₂ was 40mm in length and 15 mm in diameter, and microcracks and lamellar twins were observed in the crystals. The CuInSe₂ crystal was 55 mm in diameter, and there were many cracks in the crystal. No other work concerning the LEC has been reported in recent 20 years.

3. THM growth of I-III-VI₂ ternary compounds

3.1 Advantages of the THM growth

The traveling heater method (THM) is a growth technique in which the zone method of melt growth is applied to the solution growth, and is very useful for growing fairly large crystals and especially for growing alloy crystals with excellent composition uniformity [76]. Fig. 2 shows schematic diagrams of the bulk crystal growth. Fig. 2 (a) shows a zone melting method. A part of feed polycrystal A is melted into the zone A_L , the temperature of which is higher than the melting point of A. Crystal A' is grown from the lower portion of the zone A_L . Fig. 2 (b) exhibits a solution Bridgman method, which is a kind of solution growth methods. Feed polycrystal A and solvent B are inserted into an ampoule, and then the ampoule is heated for formation of solution $(A+B)_L$ by complete dissolution of A into B. The crystal A' is grown from the solution $(A+B)_L$ by lowering the ampoule. The growth temperature is lower than the melting point of A, but the growth temperature changes during the growth of crystal A' because concentration of the solution decreases as the growth proceeds. THM shown in Fig. 2 (c) is a growth method, where the melt A_L of the zone melting method of Fig. 2 (a) is replaced with solution $(A+B)_L$ of solute A and solvent B. Since the maximum temperature is set at the melting point of solution $(A+B)_L$, a part of feed polycrystal A dissolves in the zone. When the ampoule is lowered in the THM furnace, crystal A' is grown from the zone solution $(A+B)_L$, and the same amount of feed dissolves at the upper part of zone. Therefore, the concentration and the temperature of the solution are kept constant during the THM growth.

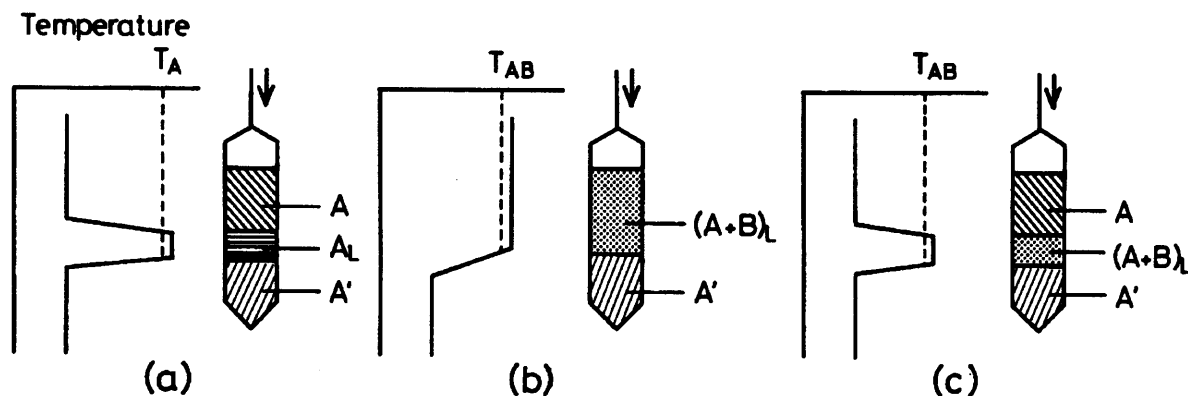


Fig. 2. Schematic diagrams of temperature profiles of the furnaces and growth features in the ampoules. (a) zone melting, (b) solution growth and (c) THM. A: feed material, A': grown crystal, B: solvent; L(subscript): liquid phase. T_A : melting point of A, T_{AB} : liquidus point of (A+B).

Advantages of the THM growth are following;

1. Growth temperature is low compared with that of the melt growth, so that decrease of the density of the intrinsic defects is expected.
2. Larger crystals can be grown compared with a conventional solution growth such as shown in Fig. 2 (b), because the amount of the solvent for THM growth is irrelevant to the length of grown crystal and is less than that for the conventional solution growth.
3. Impurities introduced from the ampoule material can be decreased.
4. The gettering effect of the solvent is expected.
5. Since the concentration and the temperature of the zone solution can be kept constant during the growth, bulk alloy crystals with a uniform composition can be grown.

The THM technique has been applied to the single crystal growth of several II-VI, III-V compounds and their alloys [76]. As for the I-III-VI₂ compounds, Mandel and co-workers performed zone growth of CuGaSe₂ from Cu₂Se-enriched melts using a horizontal furnace [48], which is considered to be the first experiment of the THM growth of I-III-VI₂ compounds, because excess Cu₂Se can be regarded as a solvent. Hsu and co-workers have obtained bulk single crystals of CuInS₂ from In solution by THM [56].

Table 2 is a list for solution growth of Cu-III-VI₂ compounds. Ga is not adequate as a solvent because CuGaS₂ and CuGaSe₂ chalcopyrite crystals cannot be precipitated from the Ga solutions up to temperatures near the melting points [7,50,66]. Since these compounds have high solubilities in In solvent and a single solid phase with chalcopyrite structure can be grown from the In solution containing stoichiometric I-III-VI₂ solute, indium

was adopted as the solvent not only for growths of the compounds containing indium as a constituent, but also for those of CuGaS_2 , CuGaSe_2 and CuGaTe_2 . Recently, growths of CuGaS_2 [46], CuGaSe_2 [49], CuGaTe_2 [53], CuInSe_2 [59,60] and CuInTe_2 [64] single crystals by THM were investigated using In solvent.

Table 2. Solution growth of Cu-III-VI₂ compounds

| Solute | Solvent | Grown crystal | Ref. |
|-------------------|-----------------|---|---------|
| CuGaS_2 | Ga | (GaS)* | [66] |
| | In | $\text{CuGa}_x\text{In}_{1-x}\text{S}_2$ | [77-79] |
| | Te | CuGaS_2 | [80] |
| | Sn | CuGaS_2 | [81,82] |
| | Pb | CuGaS_2 | [82] |
| | CdCl_2 | CuGaS_2 | [83] |
| | CdI_2 | CuGaS_2 | [83] |
| | CuI | CuGaS_2 | [84] |
| CuGaSe_2 | Ga | (GaSe)* for $T < 900^\circ\text{C}$ CuGaSe_2 for $T \geq 960^\circ\text{C}$ | [7,50] |
| | In | $(\text{Ga}_x\text{In}_{1-x}\text{Se})^{**}$ for $T < 580^\circ\text{C}$, $\text{CuGa}_x\text{In}_{1-x}\text{Se}_2$ for $T > 580^\circ\text{C}$ | [85] |
| | Te | $(\text{Cu}_2\text{Ga}_4(\text{SeTe})_7)^{***}$ | [86] |
| | Sn | (SnSe-CuGaSe ₂) two phase mixture | [7] |
| | Pb | CuGaSe_2 | [7] |
| | Bi | CuGaSe_2 | [7] |
| | CuI | CuGaSe_2 | [84] |
| CuInS_2 | In | CuInS_2 | [56,87] |
| CuInSe_2 | In | CuInSe_2 | [88,89] |
| | Bi | CuInSe_2 | [89] |
| | CuSe | $(\text{Cu}_{2-x}\text{Se}-\text{CuInSe}_2)$ two phase mixture for $T < 630^\circ\text{C}$, CuInSe_2 for $T > 630^\circ\text{C}$ | [90] |

* :Orthorhombic or hexagonal structure
 ** :Hexagonal structure
 *** :Zincblende structure

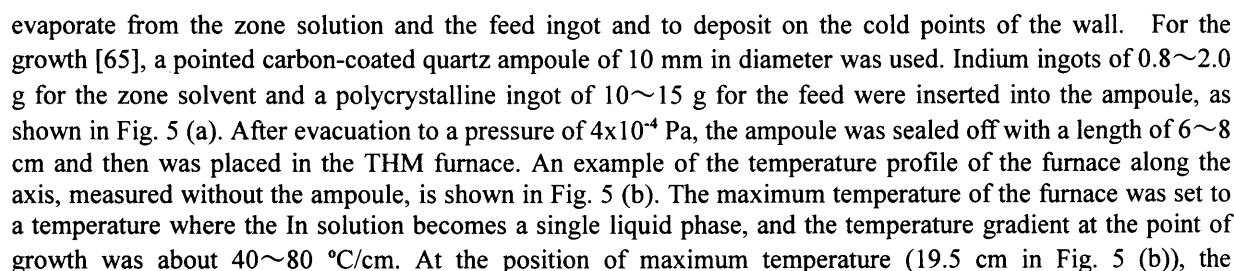
3.2 Growth of ternary compounds by THM using In solvent

The phase diagrams of CuGaS_2 -In [77-79], CuGaSe_2 -In [49,85], CuInS_2 -In [56,87] and CuInSe_2 -In [88,89] pseudobinary systems are shown in Figs. 3 (a)~(d). There exist miscibility gaps in saturated In solutions. The details for the system are described in the following.

Fig. 3 (a) shows the phase diagram of CuGaS_2 -In pseudobinary system. Indium solutions saturated with stoichiometric CuGaS_2 solutes at temperatures above 1020°C are single phase (a double line region in Fig. 3 (a)). However, those saturated below 1020°C are separated into two liquid phases (miscibility gap), and the grown crystals from the solutions always become polycrystals, because the heavier liquid phase (the secondary phase), which is deficient in sulfur and from which chalcopyrite crystals cannot be grown, remains at the bottom in the ampoule and disturbs the single crystal growth [91]. Therefore, in order to obtain a single crystal from In solution containing stoichiometric CuGaS_2 solute, the growth temperature should be kept above 1020°C . There exists a similar miscibility gap for saturated In solutions at temperatures below 850°C in the CuGaSe_2 -In system, as shown in Fig. 3 (b) [49,85]. For CuInS_2 -In and CuInSe_2 -In systems, temperatures of the boundary between single-phase and two-phase liquids are 730°C and 620°C , respectively [86-88]. Recently, CuGaTe_2 -In and CuInTe_2 -In systems were studied, and the temperatures of the boundary are 700°C and 510°C , respectively [53,64]. In consideration of the presence of a peritectic reaction in CuGaSe_2 and phase transitions in CuGaTe_2 , CuInS_2 , CuInSe_2 and CuInTe_2 in addition to the miscibility gaps, the temperature ranges of $850 \sim 1030$, $780 \sim 700$, $730 \sim 980$, $620 \sim 810$ and $670 \sim 510^\circ\text{C}$ are favorable for solution growths of CuGaSe_2 , CuGaTe_2 , CuInS_2 , CuInSe_2 and CuInTe_2 , respectively.

3.3 Growth procedure of ternary compounds

The THM growths of CuGaS_2 , CuGaSe_2 , CuGaTe_2 , CuInS_2 , CuInSe_2 and CuInTe_2 have been performed by using a vertical THM furnace with three coil heaters (Fig.4). The pre-heater was used to prevent deposition of gaseous species such as sulfur or indium sulfide on the inner wall of the ampoule. The species are likely to



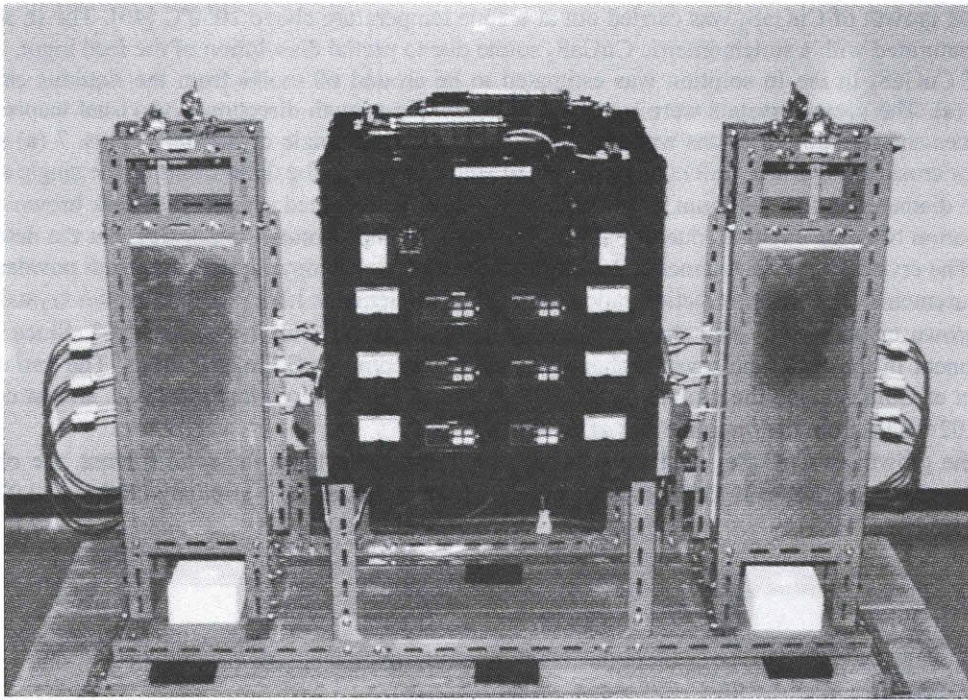


Fig. 4. Vertical THM furnaces with three coil heaters, and the temperature controllers of the furnaces. The inner diameter of the furnaces is 20 mm, and the THM ampoule is lowered at a speed of 4 mm/day by a stepping motor.

temperatures near the inner wall of the furnace (20 mm ID) were 80~150 °C higher than that at the center. Fig. 6 shows a longitudinal cross section of a sample for the THM growth of CuGaSe_2 , when the growth was stopped halfway. The shape of interface between the solution zone and the growing crystal was seen to be convex toward the solution, which is favorable for the growth of single crystals. The crystal growth was normally performed by lowering the ampoule at a speed of 4 mm/day for 10 days.

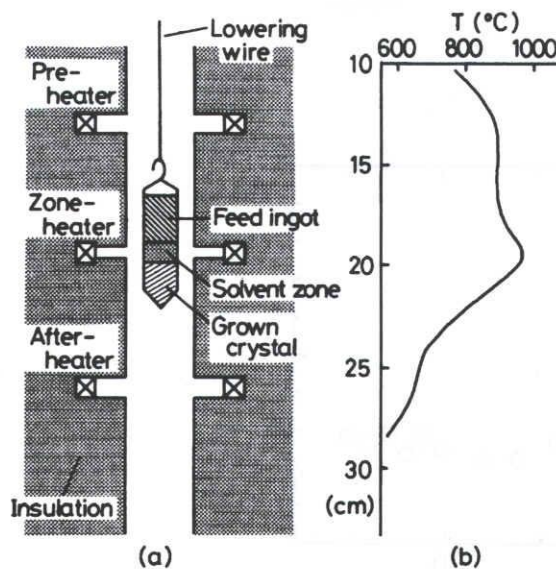


Fig. 5. (a) Schematic diagram of a THM furnace with three coil heaters. (b) Temperature profile of the furnace without an ampoule.

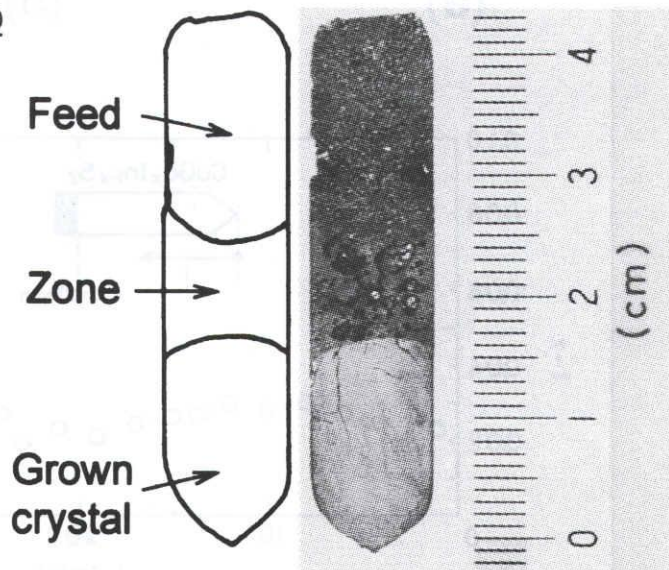


Fig. 6. Photograph of cross section of an ingot for THM growth of CuGaSe_2 , after the growth was stopped halfway. The interface between the growing crystal and the zone is convex upward.

3.4 Grown crystals of ternary compounds

The THM growth of CuGaS_2 was carried out at a zone temperature above 1050°C [46]. The In solution of the zone was saturated with a stoichiometric CuGaS_2 solute due to partial dissolution of the feed ingot, and the concentration of CuGaS_2 in the In solution was estimated to be around 60 mol% from the liquidus curve, as shown in Fig. 3 (a). The grown crystals were cut along or across the growth direction, and visual inspection of the crystal surfaces and the cross sections was used for identification of single crystallinity. Figs. 7 (a) and (b) show examples of cross sections and wafers of the obtained single crystals. The dimensions of the single crystals were 10.5 mm in diameter and 25~40 mm in length. The color of the obtained crystals was dark brown or dark orange. The variation of color might be due to optical absorption by incorporated impurities, but the details are not understood. The crystals were ascertained to be single phase with a chalcopyrite structure from powder X-ray diffraction measurements. The atomic fraction ratios of constituent elements I:III:VI in the grown crystals were 1:1:2, and the grown crystals were also shown to be $\text{CuGa}_x\text{In}_{1-x}\text{S}_2$ alloys with $1-x=0.02\sim0.03$. Since In is a dominant component in the zone, the crystals should inevitably become $\text{CuGa}_x\text{In}_{1-x}\text{S}_2$ alloys. The variation of mole fraction $1-x$ of CuInS_2 along the growth direction is shown in Fig. 8. Mole fraction $1-x$ is almost constant with values of $0.02\sim0.03$ from the tip to the end of the crystal.

As for the growth of CuGaSe_2 and CuGaTe_2 by the THM using In as the zone solvent, the obtained crystals were also $\text{CuGa}_x\text{In}_{1-x}\text{Se}_2$ and $\text{CuGa}_x\text{In}_{1-x}\text{Te}_2$ alloys with the values of $1-x=0.04\sim0.07$ and $0.07\sim0.1$, respectively [49,53].

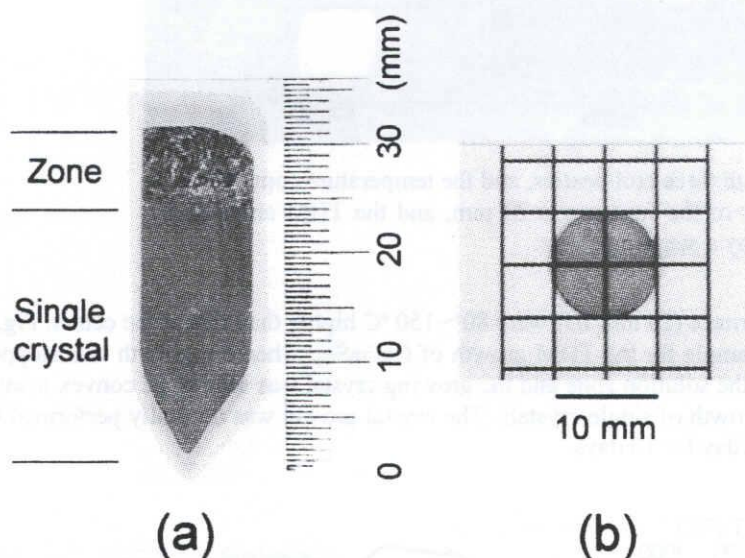


Fig. 7. Photographs of examples of the obtained single crystals for THM growth of CuGaS_2 . (a) Cross section. The end portion is the remaining zone. (b) Wafer without any grain boundary. Color of wafers was dark brown or dark orange.

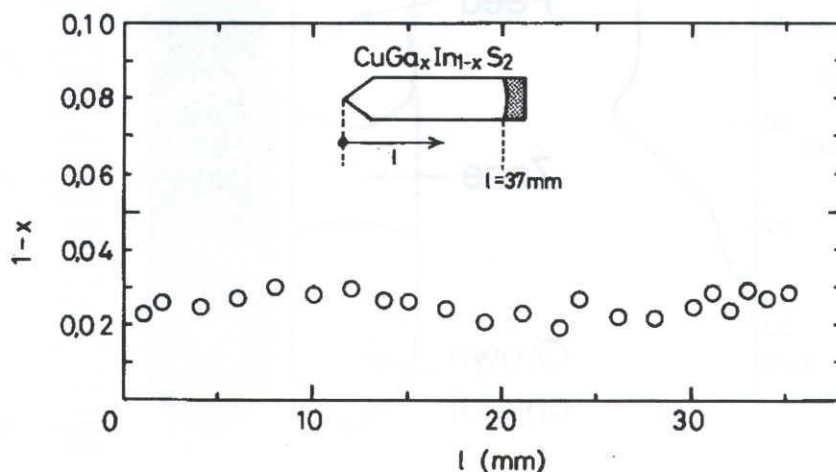


Fig. 8. The variation of $1-x$ in $\text{CuGa}_x\text{In}_{1-x}\text{S}_2$ along the growth direction of a THM-grown crystal.

Fig. 9 shows an example of cross sections of the THM-grown CuInSe_2 single crystals [59]. The growth was carried out at a zone temperature of about 750°C , and the dimensions were 10 mm in diameter and 30~35 mm in length. Figs.10 and 11 show the compositions of the crystal along and across the growth direction. It can be clearly seen that the composition of the crystal is uniform and stoichiometric.

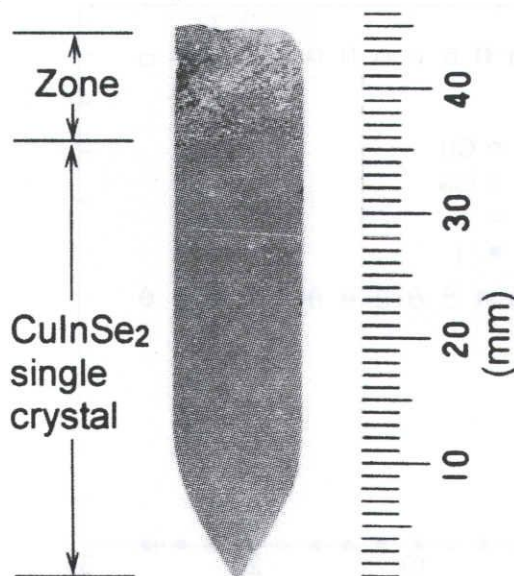


Fig.9. Photograph of an example of cross sections of the THM-grown CuInSe_2 single crystals.

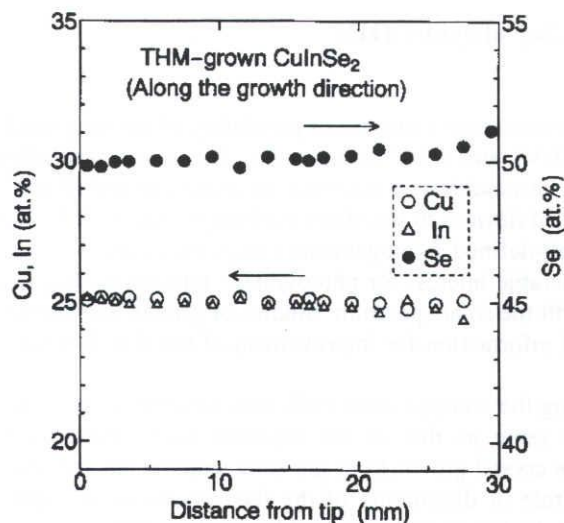


Fig. 10. Compositions of a THM-grown CuInSe_2 single crystal along the growth direction.

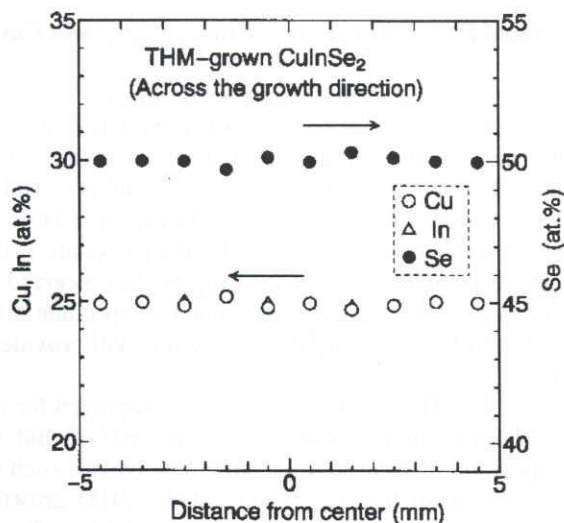


Fig. 11. Compositions of a THM-grown CuInSe_2 single crystal across the growth direction.

3.5 Growth of ternary compounds by THM using halide solvent

For the THM growth of CuGaS_2 and CuGaSe_2 using In solvent, the crystals become inevitably $\text{CuGa}_x\text{In}_{1-x}\text{S}_2$ and $\text{CuGa}_x\text{In}_{1-x}\text{Se}_2$ quaternary alloys ($1-x=0.03\sim 0.05$) by incorporation of In atoms from the solvent, as described in the previous section. However, pure CuGaS_2 crystals with 10.5 mm in diameter and 25~30 mm in length were obtained by THM using CuI solvent [47], and were shown to have nearly the same optical properties as those of iodine-CVT-grown crystals [84]. Fig. 12 shows the composition of the crystal along the growth direction. It can be clearly seen that the composition is uniform and stoichiometric and that incorporation

of iodine atoms is negligible. The greenish yellow crystals were obtained from CuI zone solution containing Ga-excess solute, but the crystals grown from Cu and Ga-excess solution showed yellow appearance.

THM growth of AgGaS₂ single crystals has been performed by using PbCl₂ solvent [43].

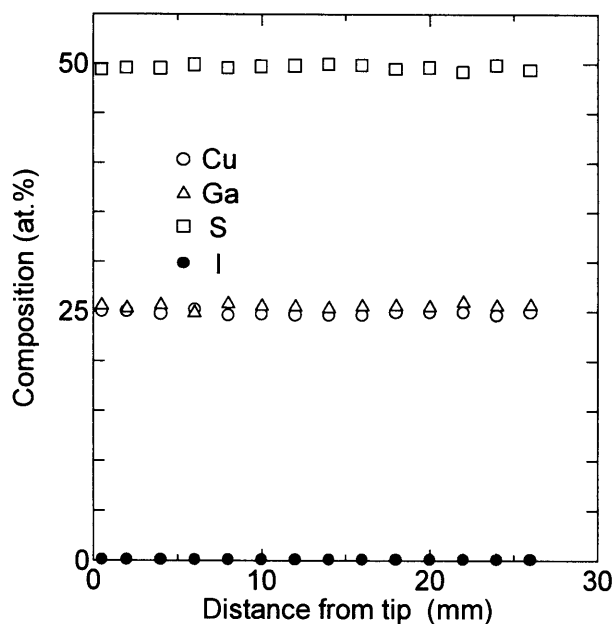


Fig. 12. Compositions of a CuGaS₂ single crystal, which is grown by THM using CuI solvent, along the growth direction.

4. Single crystal growth of CuGa_xIn_{1-x}S₂ and CuGa_xIn_{1-x}Se₂ alloys by THM

4.1 Growth procedure of quaternary alloys

The growth of I-III-VI₂ alloy crystals is also of technical interest because of possibility of tailoring band-gap energies and lattice parameters, as in the case of II-VI and III-V compounds. The quaternary alloy CuGa_{0.6}In_{0.4}S₂ is lattice-matched to ZnS, and is considered to be suitable as a substrate for epitaxy of n-ZnS layer, which is expected to be used for fabrication of lattice-matched devices in the short-wavelength region [65]. For the substrate of epitaxy, the bulk alloy crystals with a well-defined homogeneous composition are required. Another quaternary alloy CuGa_xIn_{1-x}Se₂ has received considerable interest for photovoltaic application, because its band gap can be adjusted to obtain an optimum match with the solar spectrum. Studies of growth and characterization of bulk CuGa_xIn_{1-x}Se₂ crystals will provide useful information for improvement of the thin film solar cells.

The THM technique has been employed for obtaining the homogeneous bulk alloy crystals. In the alloy growth, the composition of feed material should be the same as that of the required alloy crystal. The composition of zone solution should be chosen such that the crystal grown from the zone solution has the alloy composition. In the steady state of the THM growth, the rate of dissolution of the feed crystal at the upper interface of the zone is the same as that of crystallization at the lower interface, and hence the compositions of zone solution and the grown alloy crystal are kept constant during the growth run.

Figs.13 and 14 show solidus curves for the In solutions containing 60 mol% CuGa_xIn_{1-x}S₂ and CuGa_xIn_{1-x}Se₂ solutes ($x=0\sim 1$) [92,93]. In order to obtain CuGa_xIn_{1-x}S₂ and CuGa_xIn_{1-x}Se₂ single crystals of uniform compositions x by THM, the In solutions containing CuGa_yIn_{1-y}S₂ and CuGa_yIn_{1-y}Se₂ solutes of composition y corresponding to x must be used for the zones.

For THM growth of the alloys with x , In solutions containing 60 mol% CuGa_yIn_{1-y}S₂ or CuGa_yIn_{1-y}Se₂ were prepared with 0.8~1.0 g of elemental In as a solvent, and then the solutions were quenched to room temperature. The obtained ingot was charged as zone material at the bottom of an ampoule, and polycrystalline CuGa_xIn_{1-x}S₂ or CuGa_xIn_{1-x}Se₂ as a feed material was put on it. For the growth of sulfide, a small amount of sulfur (0.1~0.3 g) was added in the ampoule in order to suppress evaporation of sulfur from the zone and feed. The vacuum-sealed ampoule was placed in a vertical THM furnace, and the THM growth was started.

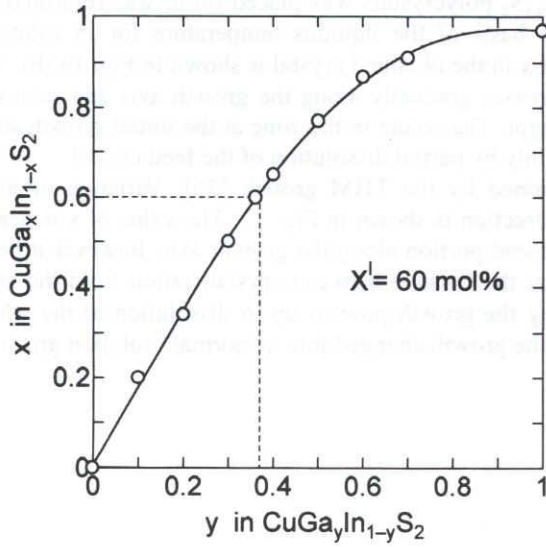


Fig. 13. Solidus curve of $\text{CuGa}_x\text{In}_{1-x}\text{S}_2$ -In system crystals. x of $\text{CuGa}_x\text{In}_{1-x}\text{S}_2$ crystals, grown from In solutions containing 60 mol% $\text{CuGa}_y\text{In}_{1-y}\text{S}_2$ pseudo-solute, is shown as a function of y .

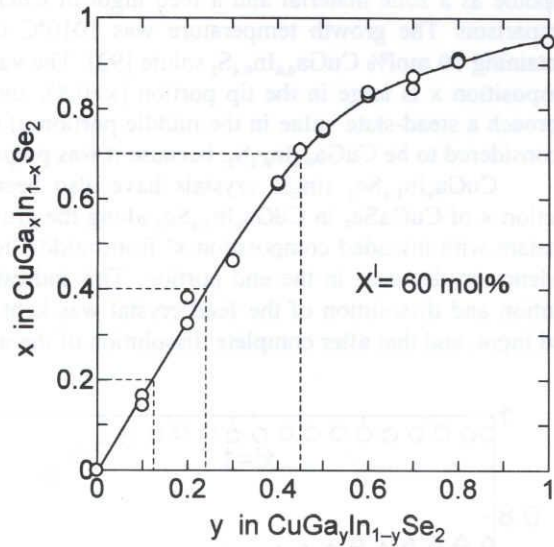


Fig. 14. Solidus curve of $\text{CuGa}_x\text{In}_{1-x}\text{Se}_2$ -In system. x of $\text{CuGa}_x\text{In}_{1-x}\text{Se}_2$ crystals, grown from In solutions containing 60 mol% $\text{CuGa}_y\text{In}_{1-y}\text{Se}_2$ pseudo-solute, is shown as a function of y of the solute.

4.2 Grown crystals of quaternary alloys

Figs. 15 (a) and (b) show an example of $\text{CuGa}_{0.6}\text{In}_{0.4}\text{S}_2$ single crystals obtained by the THM growth, whose zone was In solution with 60 mol% $\text{CuGa}_{0.37}\text{In}_{0.63}\text{S}_2$ solute, and its longitudinal cross section, respectively [65]. The variation of mole fraction x of CuGaS_2 in $\text{CuGa}_x\text{In}_{1-x}\text{S}_2$ along the growth direction is shown in Fig. 16 (a). The value of x is nearly constant with $x=0.6$ from the tip to 25 mm along the growth axis, but it has a tendency to decrease in the end region. This indicates that the balance between crystallization from the zone solution and dissolution of the feed crystal was kept during the growth process up to dissolution of the whole feed ingot. A few experiments of the THM growth, where only In was initially charged at the bottom of the

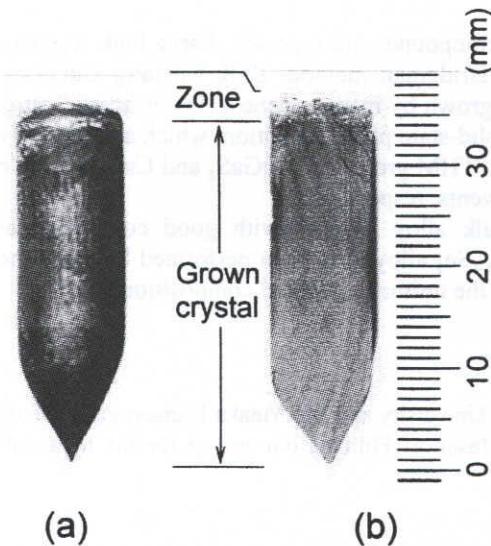


Fig. 15. Photographs of examples of the crystals grown by THM using zones of In solution containing 60 mol% $\text{CuGa}_{0.37}\text{In}_{0.63}\text{S}_2$ pseudo-solute. (a) Ingot, (b) Cross section. The end portion is the remaining zone.

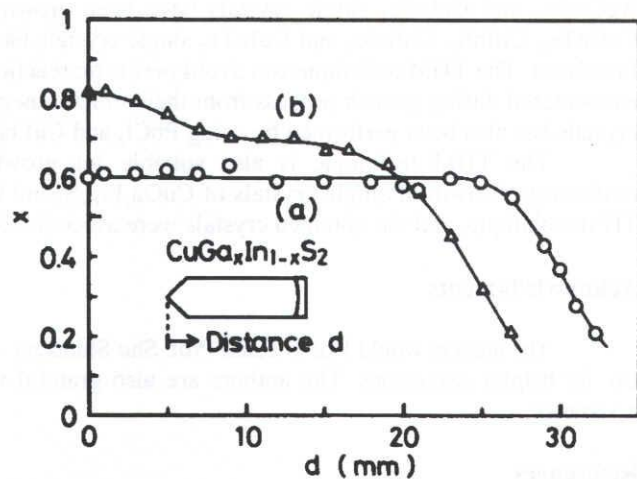


Fig. 16. Variation of composition x in THM-grown $\text{CuGa}_x\text{In}_{1-x}\text{S}_2$ crystals along the growth directions. The initial compositions of solutes in the zone solutions were (a) $\text{CuGa}_{0.37}\text{In}_{0.63}\text{S}_2$ and (b) $\text{CuGa}_{0.6}\text{In}_{0.4}\text{S}_2$, and the initial solute concentrations were 60 mol%.

ampoule as a zone material and a feed ingot of $\text{CuGa}_{0.6}\text{In}_{0.4}\text{S}_2$ polycrystals was placed on it, was reformed for comparison. The growth temperature was 1010°C on the basis of the liquidus temperature for In solutions containing 60 mol% $\text{CuGa}_{0.6}\text{In}_{0.4}\text{S}_2$ solute [92]. The value of x in the obtained crystal is shown in Fig. 16 (b). The composition x is large in the tip portion ($x > 0.8$), and decreases gradually along the growth axis and seems to approach a steady-state value in the middle portion of the ingot. The solute in the zone at the initial growth stage is considered to be $\text{CuGa}_{0.6}\text{In}_{0.4}\text{S}_2$, because it was prepared only by partial dissolution of the feed crystal.

$\text{CuGa}_x\text{In}_{1-x}\text{Se}_2$ single crystals have also been obtained by the THM growth [36]. Variation of mole fraction x of CuGaSe_2 in $\text{CuGa}_x\text{In}_{1-x}\text{Se}_2$ along the growth direction is shown in Fig. 17. The value of x is nearly constant with intended composition x' from middle to near-end portion along the growth axis, however it has a tendency to decrease in the end portion. This indicates that the balance between crystallization from the zone solution and dissolution of the feed crystal was kept during the growth process up to dissolution of the whole feed ingot, and that after complete dissolution of the ingot, the growth changed into a "normal" solution growth.

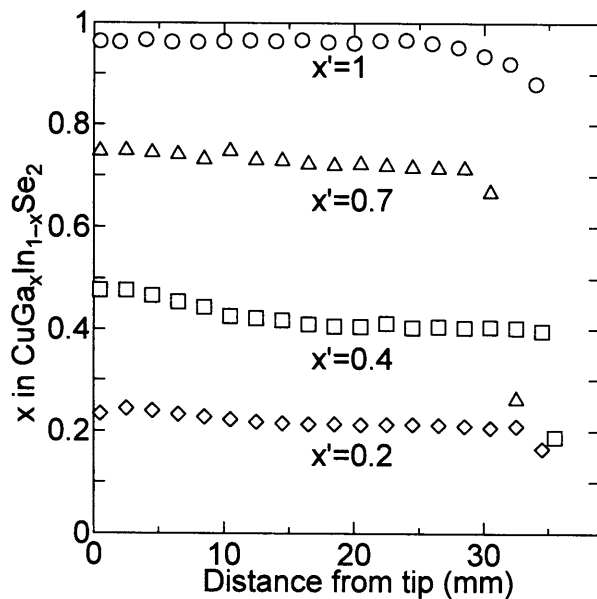


Fig. 17. Variation of composition x in THM-grown $\text{CuGa}_x\text{In}_{1-x}\text{Se}_2$ crystals along the growth directions. The intended compositions x' are 0.2, 0.4, 0.7 and 1.

5. Conclusion

The bulk single crystals of I-III-VI₂ chalcopyrite ternary compounds are reported. Large bulk AgGaS_2 , AgGaSe_2 , and CuInSe_2 single crystals have been grown by the Bridgman method. Bulk CuGaS_2 , CuGaSe_2 , CuGaTe_2 , CuInS_2 , CuInSe_2 , and CuInTe_2 single crystals have been grown by means of the THM technique using In solvent. The THM technique can avoid peritectic reaction and solid-state phase transition, which are generally encountered during growth process from their stoichiometric melts. THM growth of AgGaS_2 and CuGaS_2 single crystals has also been performed by using PbCl_2 and CuI halide solvents, respectively.

The THM technique is also suitable for growth of bulk alloy crystals with good compositional uniformity. Growth of single crystals of $\text{CuGa}_x\text{In}_{1-x}\text{S}_2$ and $\text{CuGa}_x\text{In}_{1-x}\text{Se}_2$ alloys has been performed by using the THM technique, and the obtained crystals were ascertained to have the uniform intended compositions.

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