

## The Growth of $p$ -Type $A^{III}B^{III}C_2^{VI}$ Single Crystals

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### Abstract

$A^{III}B^{III}C_2^{VI}$  single crystals were grown by the modified Bridgman-Stockbarger method, a procedure similar to direct freezing in our crystal growth laboratory.  $A^{III}B^{III}C_2^{VI}$  compounds are collected into two groups (III. group: Tl, Ga, In and VI. group: Se, S, Te): 1. TlGaSe<sub>2</sub>, TlGaS<sub>2</sub> and TlInS<sub>2</sub> have layer structure. 2. TlInSe<sub>2</sub>, TlInTe<sub>2</sub> and TlGaTe<sub>2</sub> have chained structure. The main reasons such crystals grown with this method is similar to the direct freezing method because 1) quality of crystals is the same as crystals grown by other methods, and 2) growth time of crystals is shorter by about 5-10 days. None of the grown crystals had cracks and voids on the surface. Freshly cleaved crystals had a mirror-like surface and there was no need for mechanical or chemical polishing. The X-ray Laue back reflection method was used to test the crystallinity of the prepared samples. It was found that the crystals was  $p$ -type by hot probe technique. The ingots produced were single crystals and the useful region of single crystal was approximately 90% of the bulk.

**Key Words:**  $A^{III}B^{III}C_2^{VI}$  compounds, furnace, ampoule shapes, crystal growth laboratory, layer and chained structure, single crystal.

### Introduction

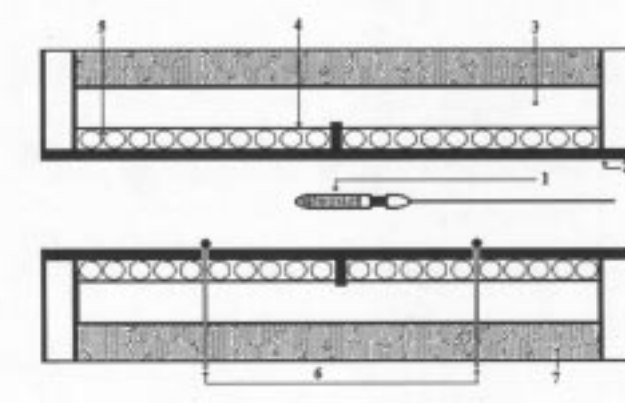
$A^{III}B^{III}C_2^{VI}$  compounds are formed in the layered-chain structure as  $A^{III}B^{III}C_2^{VI}$  in which the components  $A^{III}C^{VI}$  and  $B^{III}C^{VI}$  have the ratio 1:1. For instance, in the compound TlGaSe<sub>2</sub>, the components are arranged in the form GaSe-TlSe and they are called the “Ternary layered TlGaSe<sub>2</sub>-type Chalcogenides”. In recent growing interest has been paid to the physics of one-dimensional and two-dimensional systems. The latter are represented vividly by  $A^{III}B^{III}C_2^{VI}$  crystals, such as TlGaSe<sub>2</sub>, TlInSe<sub>2</sub> and TlInS<sub>2</sub>. These crystals are characterized by a clearly defined anisotropy of mechanical properties. The compound TlGaSe<sub>2</sub> falls under the category of new incomplete-valance  $A^{III}B^{III}C_2^{VI}$  type semiconductors. Some of their electrical, photoelectrical and optical

properties are well explored in a number of publications [1-9].

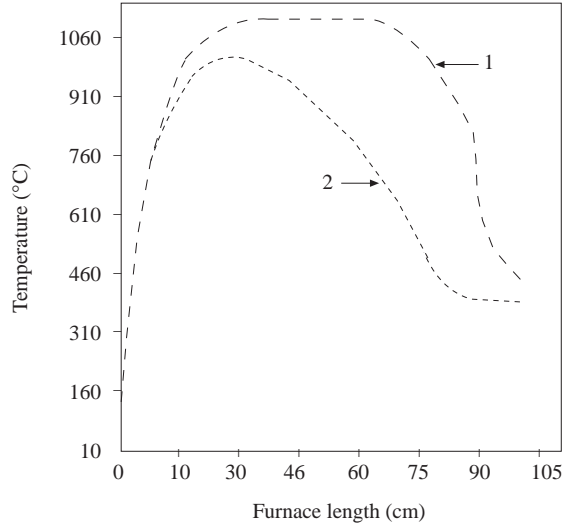
Crystals of the solid solution system of  $TlGa_xIn_{1-x}Se_{2x}S_{(1-x)}$  were grown by the Bridgman-Stockbarger method in evacuated quartz ampoules [10]. Measurements of the absorption spectra of  $TlGaS_{2x}Se_{(1-x)}$  solid solutions have been obtained at temperatures from 110 to 300 K, and it has been long concluded that the long-wave region of the edge absorption corresponds to indirect optical transitions [11]. p-type  $TlGaSe_2$  crystals were prepared by the Bridgman-Stockbarger method in [12-14]. Large crystals of  $TlGaSe_2$  were grown via the Bridgman method in [15]. Good quality single crystals have generally been obtained from non-stoichiometric melts using the Bridgman [16] and Czochralski [17] techniques. But recently, small samples have been grown from the vapour phase by chemical transport process [18].  $TlGaSe_2$ ,  $TlInSe_2$  ( $Te_2$ ) and  $TlGaTe_2$  compounds have melting point of  $820\pm 5$  °C [19],  $767\pm 5$ °C,  $772\pm 5$ °C and  $773\pm 5$  °C [2], respectively.  $A^{III}B^{III}C_2^{VI}$  single crystals were grown by the modified Bridgman-Stockbarger and a method similar to direct freezing method, in our crystal growth laboratory.

## 2. Experimental Procedures

The horizontal furnace used in this work consists of two zones, each with an alumine tubes 50 cm in length as shown in figure 1. The furnace was heated using kanthal DSD (Cr-Al-Fe) heating elements. The temperature of each zone was monitored by K-type (Cromel-Alumel) thermocouples positioned close to the middle of the zone. Two thermocouples were used to control the stability of temperature in the region of growth. A stable temperature gradient of about 23 cm was established between the two zones. The temperature gradient is given in Figure 2.



**Figure 1.** The horizontal furnace. 1. Quartz rod, 2. Alumina tube, 3. Zirconium blanket for insulation, 4. Aluminium foil, 5. Heating element (Cr-Al-Fe), 6. Thermocouples, 7. Air pocket.



**Figure 2.** The temperature gradient of growth furnace. 1. Each zone of growth furnace was set to 1000 °C, and then allowed to equilibrate, 2. The first zone of growth furnace was set to 1000°C, second zone was set to 700 °C, with the temperature gradient between them.

The choice of a growth technique for a particular material depends on many factors which may be summarized as follows:

a) The chemical reactivity of the compound and constituent the elements. b) The dissociation vapour pressure of the compound at the growth temperature. c) The melting point of the compound and whether the compound and whether the compound melts congruence or not. d) Presence or absence of phase transformations.

For the constituent of polycrystalline  $A^{III}B^{III}C_2^VI$ , the basic elements rather than the binary compounds were used due to purity considerations. These elements were weighed in a stoichiometric ratio accurate to 0.1 mg. The mass of elements was standardized to about 50 g, the basic criteria for this choice being, firstly, to yield a sufficient amount to justify cost of one run and, secondly, minimize the loss of material in case of breakage. This stoichiometric ratio necessary to produce 50 g  $TlGaSe_2$  was calculated using the following relationships:

$$M_{Tl} = (M_{Ga}/A_{Ga})A_{Tl} \quad (1)$$

$$M_{Se_2} = 2(M_{Ga}/A_{Ga})A_{Se} \quad (2)$$

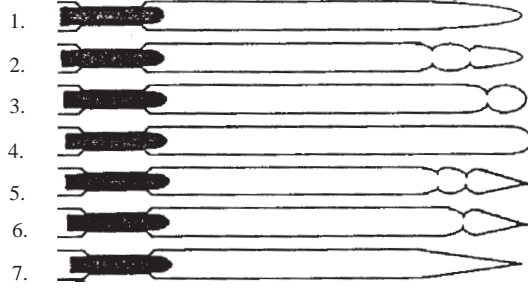
with total mass,

$$M(Ga) + M(Tl) + M(Se) = 50g. \quad (3)$$

Where, M and A are total and atomic masses, respectively. The Gallium element was weighed as the first element because of the hardness of the material and the difficulty in which it is to cut Gallium to desired accuracy limits.

$A^{III}B^{III}C_2^{VI}$  compounds consist of two groups (III. group: Tl, Ga, In and VI. group: Se, S, Te): 1. TlGaSe<sub>2</sub>, TlGaS<sub>2</sub> and TlInS<sub>2</sub> have layered structure, and 2. TlGaSe<sub>2</sub>, TlGaTe<sub>2</sub> and TlGaSe<sub>2</sub> have a chained structure.

The quartz ampoules, which are illustrated in Figure 3, have been formed according to the structure (layer-chain) of growth crystals. Ampoules numbered 1, 2, 3, and 4 were used to grow layered structures (TlGaSe<sub>2</sub>, TlGaS<sub>2</sub> and TlInS<sub>2</sub>) and those numbered others 5, 6 and 7 were used to grow chained structures (TlInSe<sub>2</sub>, TlInTe<sub>2</sub> and TlGaTe<sub>2</sub>). The quartz ampoules used in the growth process were shaped and carbon-coated in our crystal growth laboratory. The general procedure for cleaning the ampoules was follows:



**Figure 3.** Typical ampoule shapes.

i. The ampoules were cleaned with diluted HNO<sub>3</sub> for four hours in order to remove metallic contamination on the surface.

ii. Each were then rinsed repeatedly with deionised water.

iii. Each was soaked in liquid jell for 30 hours and rinsed again with deionised water to remove dust particles or grease on the inner surface of the ampoule.

iv. The inner and outer surface of the ampoules were etched with HF (45 % diluted) for 6 minutes to help further removal of any residual contaminations.

v. The ampoules were once again rinsed with deionised water, washed with acetone and left to dry.

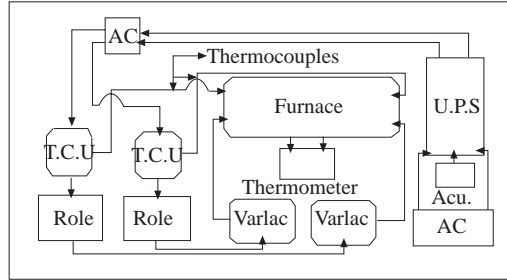
vi. The ampoules in outgass furnace were baked at 1050 °C for 30 hours in order to outgass of them.

vii. Each ampoule was ultrasonically washed in deionised water.

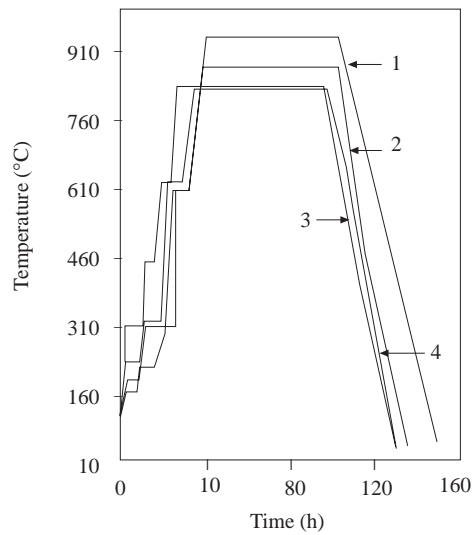
### 3. Result and Discussion

p-TlGaSe<sub>2</sub>, p-TlInSe<sub>2</sub>, p-TlInTe<sub>2</sub>, p-TlGaTe<sub>2</sub>, p-TlGaSe<sub>2</sub>:Dy (Dy: Dysprosium), p-TlIn<sub>0.3</sub>Ga<sub>0.7</sub>Se<sub>2</sub> and p-TlIn<sub>0.5</sub>Ga<sub>0.5</sub>Se<sub>2</sub> single crystals were grown by the modified Bridgman-Stockbarger method in our crystal growth laboratory. p-Tl<sub>0.999</sub>GaPr<sub>0.001</sub>Se<sub>2</sub> (Pr: Praseodymium), p-TlGa<sub>0.995</sub>Pr<sub>0.005</sub>Se<sub>2</sub>, p-TlGa<sub>0.999</sub>Pr<sub>0.001</sub>Se<sub>2</sub> and p-TlGaSe<sub>2</sub>:Gd

single crystals were grown by a method which is similar to direct freezing method. In this method, the horizontal furnace and quartz ampoule having the elements are stable. The temperature of furnace is increased step by step paying attention to melting point of grown crystal and of using elements when the necessary temperature is obtained to grow crystals. The temperature of growth furnace is decreased to room temperature step by step paying attention to phase transition temperature. A schematic of the overall system is shown in Figure 4. The crystal growth system has continuous working characteristic, and has been controlled from both zones of the furnace. Temperature within the furnace was controlled via a variac and the velocities (times) were controlled setting by a T.C.U.

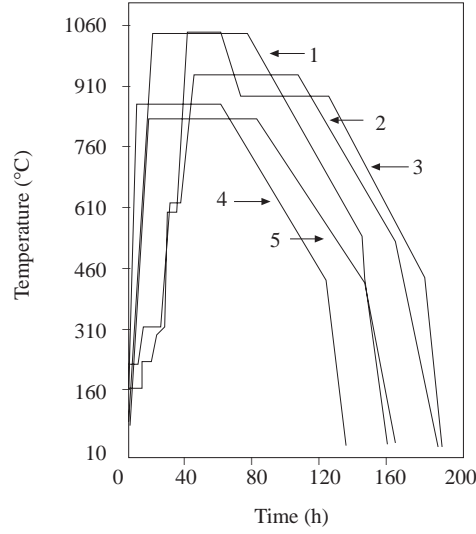


**Figure 4.** Schematic appearance of growth system. (T.C.U): Temperature Control Unit, (U.P.S): Uninterruptible Power Supply.



**Figure 5.** Programme for prereaction. 1. p-TlGaSe<sub>2</sub>:Dy, 2. p-TlGaSe<sub>2</sub>, 3. p-TlInTe<sub>2</sub> and TlGaTe<sub>2</sub>, 4. TlInSe<sub>2</sub>.

The prepared  $A^{III}B^{III}C_2^{VI}$  single crystal ingots were about 12 mm in diameter and about 70 mm in length. A sealed quartz ampoule was annealed at 1020 °C for 10 hours in the outgassing furnace designed in our laboratories. The temperature of quartz ampoule was decreased to room temperature in 7 hours. For example, the typical Bridgman-Stockbarger growth procedure of  $\text{TlGaSe}_2$  is as follows. A stoichiometric mixture of Tl-Ga-Se-Se was put into the quartz ampoule and sealed under a vacuum of 10–6 mbar. The crucible (13 mm in diameter and about 250 mm in length) was suspended in the middle of the horizontal furnace. The other crystals were grown in a similar way. Pre-reaction and growth programmes of all grown crystals are given in Figure 5 and 6, respectively. The melting temperatures of the constituents were considered in pre-reaction with growth programme and the temperature was stabilized for completing the reaction between the elements. As seen in Figure 6, the pre-reaction process did not apply to p-Tl<sub>0.999</sub>GaPr<sub>0.001</sub>Se<sub>2</sub>, p-TlGa<sub>0.995</sub>Pr<sub>0.005</sub>Se<sub>2</sub>, p-TlGa<sub>0.999</sub>Pr<sub>0.001</sub>Se<sub>2</sub> and p-TlGaSe<sub>2</sub>:Gd

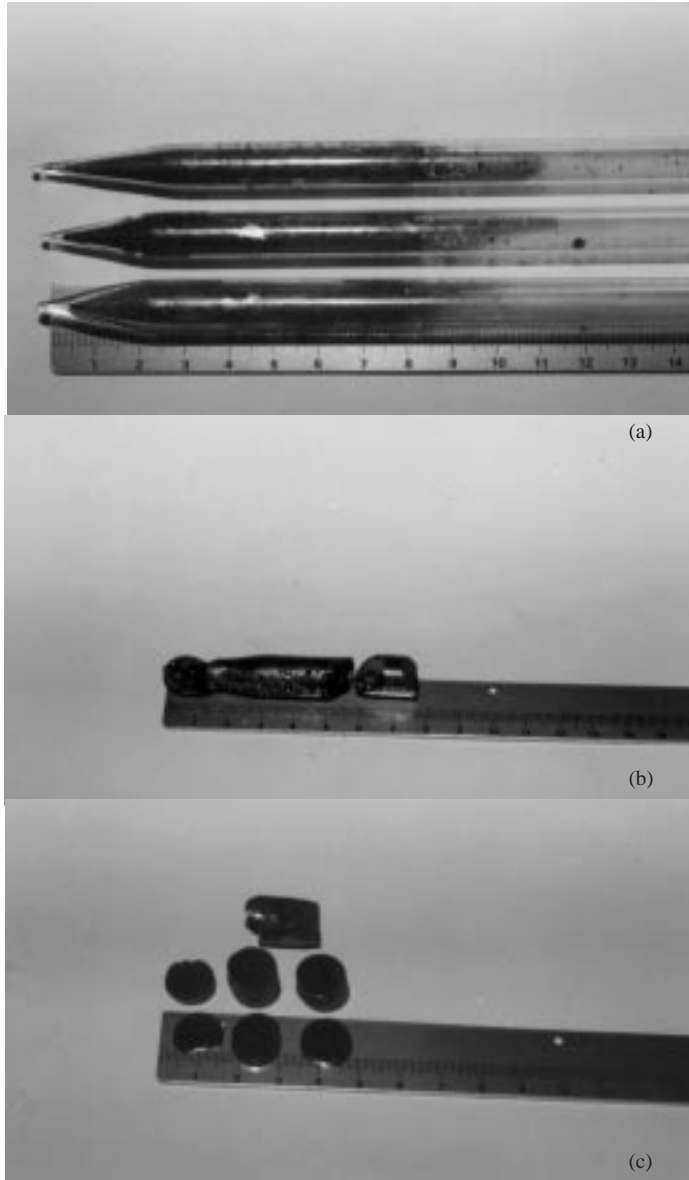


**Figure 6.** Growth programme for single crystals.

1.  $\text{TlGaSe}_2:\text{Dy}$ , 2.  $\text{Tl}_{0.999}\text{GaPr}_{0.001}\text{Se}_2$ ,  $\text{TlGa}_{0.995}\text{Pr}_{0.005}\text{Se}_2$  and  $\text{TlGa}_{0.999}\text{Pr}_{0.001}\text{Se}_2$
3. p-TlGaSe<sub>2</sub>:Gd, 4.  $\text{TlGaSe}_2$ ,  $\text{TlIn}_{0.3}\text{Ga}_{0.7}\text{Se}_2$  and  $\text{TlIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ , 5.  $\text{TlInSe}_2$ , p-TlGaTe<sub>2</sub> and  $\text{TlInTe}_2$ .

The none of the grown crystals had cracks and voids on the surface. The freshly cleaved crystals have a mirror-like surface and there is no need for mechanical or chemical polishing treatments. Samples for experiments were cleaved along the cleavage planes (001). The X-ray Laue back reflection method was used to test the crystallinity of the prepared samples. It was found that the crystals was p-type by hot probe technique [20]. Absorption measurements obtained from crystals grown in our laboratory are given also Table 1. The absorption properties of Dy doped and undoped p-type p-TlGaSe<sub>2</sub> have

been made by Gürbulak [21].



**Figure 7.** The photographic appearance of  $A^{III}B^{III}C_2^{VI}$  bulk crystal: (a) in the crucible, (b) out of the crucible and (c) cleaved  $TlGaSe_2$  crystals.

**Table 1.** Direct and indirect band gap values of  $A^{III}B^{III}C_2^{VI}$  samples versus sample temperatures.

Samples	Direct band gap			Indirect band gap		
	$E_{gd}(eV)$			$E_{gi}(eV)$		
	10 K	100 K	300 K	10 K	100 K	300 K
p-TlGaSe <sub>2</sub>	2.230	2.221	2.165	2.162	2.152	2.110
p-TlGaSe <sub>2</sub> :Gd	2.272	2.263	2.189	2.161	2.151	2.096
p-TlGaSe <sub>2</sub> :Dy	2.294	2.275	2.223	2.152	2.113	2.105
p-TlGa <sub>0.999</sub> Pr <sub>0.001</sub> Se <sub>2</sub>	2.219	2.209	2.142	2.201	2.173	2.109
p-Tl <sub>0.999</sub> GaPr <sub>0.001</sub> Se <sub>2</sub>	2.237	2.228	2.164	2.172	2.164	2.122
p-Tl <sub>0.995</sub> Pr <sub>0.005</sub> Se <sub>2</sub>	2.245	2.234	2.155	2.211	2.204	2.128
p-TlIn <sub>0.3</sub> Ga <sub>0.7</sub> Se <sub>2</sub>	2.158	2.141	2.098	2.130	2.111	2.064
p-TlIn <sub>0.5</sub> Ga <sub>0.5</sub> Se <sub>2</sub>	2.107	2.095	2.019	2.090	2.074	2.004

The reason the crystal growth is similar that obtained via the direct freezing method is:

- The quality of crystals is the same as crystals grown by another methods (modified Bridgman/Stockbarger, Bridgman, Stockbarger, and Czochralski technique etc.),
- Growth time of crystals is shorter by about 5-10 day,
- The growth is easy and efficiency.

The investigated method, which is similar to the direct freezing method, reproducibly yielded numerous single crystal samples, that required a total growth time of 5-18 days. The ingots produced were single crystal with approximately 90% of the bulk useful (see Figure 7). The following procedures must be applied so quality crystals may be grown:

- Components must have high purity (6N: 99.9999%);
- Ampoules must be clean;
- Ampoules must be formed according to crystals structure (chain, layer);
- Ampoules must be coated with carbon;
- Pressure in the ampoules must be very low ( $10^{-5}$ - $10^{-9}$ mbar);
- It must be known that elements react with ampoules or not;
- If there is phase transient of crystals, vapour and melt point of the elements must be known;
- Crystal properties must be known very well.

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