CHAPTER 2

Growth of GeSePb_x (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4) Single Crystals


2.1 INTRODUCTION

The use of crystals has a long documented history and has been present in practically every culture and religious tradition. They were used in Biblical times, throughout Ancient Egypt, Rome and date to all ancient cultures. Over the years, uses for crystals have not really changed and they are still being used in the same way as the ancients. However, we do now have the modern-day benefit of discoveries such as the silicon chip for computer technology and quartz to power clocks and watches. Crystals are used by scientists in emergent technological fields such as holographic computers. Crystals are particularly valuable for their amplifying and absorbing properties, as well as their pronounced ability to conduct energy from one source to another.

The actual word crystal comes from a Greek word Crystallos, from “Krysos” meaning “ice cold”, as it was originally thought that crystals were a type of ice that was so cold it would never melt [1].

On hearing the word “crystal,” most of us call up images of regular, symmetric forms, perhaps the prismatic form of rock-crystal, or the dendritic form of snow crystals. We use the term “crystal clear” to imply something transparent and pure. The ancient Greeks used the term crystal (‘κρυστάλλο’) to imply clear, transparent, and hard ice; rock-crystal was so named as it was thought to be unmeltable ice that existed in fissures of rocks. As in the present day, the regular polyhedral forms were the ones that roused the most interest. Pythagoras, for example, used the word crystal to imply perfection, harmony, and beauty; and Plato listed his famous five polyhedra, related to fire, earth, air, water, and the universe. Around the late 1700’s this theory was superseded by the idea that crystals “grew” by the addition of layers. Now science has been able to calculate physical laws which clarify this theory. When a crystal is shattered, each piece may vary in size, but the fragments all have the same shape.

The history of crystallography really began in 1669 when Nicolaus Steno noticed that quartz crystals, no matter where they came from or what size they were, always had the same set of characteristic angles between their faces. In 1912 Sir William Lawrence Bragg and his father Sir William Henry Bragg discovered that crystalline solids produced surprising patterns of reflected X-rays. They found that
crystals produce certain specific wavelengths and incident angles or intense peaks of reflected radiation, now known as Bragg peak.

Fundamental aspects of crystal growth had been derived from early crystallization experiments in the 18th century. Theoretical understanding starting with the development of thermodynamics in the late 19th century [2] and with the development of nucleation and crystal growth theories and the increasing understanding of the role of transport phenomena in the 20th century. The Phenomena of under cooling supersaturating and the heat of crystallization were already recognized in the 18th century by Fahrenheit and Philos [3].

The evolution of our knowledge of crystal growth requires not only scientific understanding, but the driving force of applied technology which so often provides a significant influence in highlighting our lack of scientific knowledge and the need for a more refined science and indeed the development of new concepts. Crystal growth now embraces an immense field of materials and technologies, which could not be covered in-depth by any one book. Nevertheless the present selection of chapters does provide a comprehensive coverage, which has succeeded in advancing our knowledge of the latest developments in crystal growth.

Interest and understanding of the morphology of crystals which started in the 17th century, independently one of dendritic forms and the other of polyhedral forms bounded by flat faces, have now advanced to a state to be understood from a unique viewpoint, the atomistic process of crystal growth. This is due to the development of the science of crystal growth in the 20th century, particularly after the 1950's. For simple and pure model systems, it is now possible to explain at the atomistic level why and how the same crystal can take a variety of forms, from dendritic, hopper, to polyhedral forms, and why different crystal species exhibit different characteristic forms or Habitus. How our understanding of morphology and growth mechanism of crystals has developed since the time of Kepler and Steno has recently been summarized by Sunagawa [4].

Snow crystals and rock crystals are naturally formed crystals under uncontrolled, fluctuating, and often sharply changing growth conditions. Any mineral crystals constituting the solid earth and planetary bodies were formed under such conditions and in impure, complicated, and complex systems. Also inorganic and
organic crystals are formed in various organs and cells of animate bodies, through biological processes necessary to sustain life or to eliminate unnecessary waste compounds. How crystals nucleate and grow, and how their forms are controlled in such complicated and complex systems are problems still waiting for proper answers at the atomistic level. The temperature and pressure conditions of mineral formation have been estimated based on equilibrium thermodynamics and phase relations. Information about conditions of mineral formation may be obtainable assuming that any geological systems have already reached the equilibrium state. However, crystals can neither nucleate nor grow under equilibrium condition. Driving forces, namely conditions deviating from the equilibrium state, are necessary to realize nucleation and growth of crystals. In natural crystallization, growth rates may fluctuate or abruptly change during their growth processes, and morphology and element partitioning are influenced accordingly. Crystals may be partially dissolved during the process of formation, or experience transformation in their post growth histories.

We are unable to observe in situ the growth or post growth process of mineral formation, but we can investigate samples that experienced these processes, provided that these processes are recorded in the samples in some form and can be visualized by appropriate methods. In nearly perfect single crystals, these are recorded in the form of various physical imperfections and chemical heterogeneities, preserving the records of morphological evolution during the growth or post growth processes. Information obtainable from such samples is equally important and informative in understanding the formation of solid earth and planetary materials, provided that such information can be evaluated properly.

Natural crystals of many materials are available in nature but they cannot be used directly for devise applications. Instead they should give some sort of treatment because of the main problem of purity and perfection. The crystal growth study in last 10 years [5 - 9] led to the conclusion that the artificial crystals of most of the materials can be grown in laboratories. To satisfy the modern days need of science and technology the crystals are produced artificially crystal. The crystal growth processes have been described in many books [10-22].

The metal dichalcogenides assumed to have layered structure. Among the layered compounds, dichalcogenides have been recognised as an ideal model
compounds for the studies involving surfaces, Photoreactions, adsorption phenomena, catalysis, scanning tunnelling microscopy, spectroscopy and epitaxial growth of thin films. The extremely anisotropic character of the layer compounds built in at atomic level dominates all the properties of such materials, both mechanical and electrical. It opens up new opportunities for the application of layered materials. The potential of this class of materials has not been fully explored yet but appears to be limited mainly by the availability of suitable materials. Attempts have been made to produce good quality crystals and thin films of layered semiconductors for different uses.

Present work has been concentrated on the growth of GeSePb_x (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4) single crystals for comparison and contrast.

2.2 DIFFERENT METHODS FOR CRYSTAL GROWTH

Crystal growth, in principle, involves controlled phase transformation from disordered fluid phase to with high atomic mobility and hence we may define four categories of crystal growth processes. Different methods for crystal growth are classified as below:

1. Vapour Growth : Growth form the vapour phase
2. Solution Growth : Growth from an aqueous solution
3. Melt Growth : Growth from a supercritical or fluid Phase
4. Solid Growth : Growth from one or more solid Phases

These techniques are adequately described in various text books and reviews [23- 46]. Figure 2.1 shows these main categories with their subfamilies.

From the literature survey it has been found that many materials have been grown using different techniques. The choice of technique basically depends upon the properties of the material to be synthesized. Materials in crystalline form required in modern devices need to be of high purity, high degree of perfection with minimum defects. Most of the basic techniques of crystal growth and their modification are described at length by Brice [47] and Peiser [48].
Figure 2.1: The various types of crystal growth techniques.

Single crystal of GeSePb$_x$ (DVT) ($x = 0, 0.1, 0.2, 0.3, 0.4$) are not available in nature so they have to be synthesized in the laboratory. These compounds having layered structure are insoluble in water and decomposed before their melting point is reached. They sublime at higher temperature; hence the growth of single crystals of such compounds from melt and aqueous solution is also not possible. The vapour transport method offers the advantage of growth at lower temperature below their melting point and found to be most suitable for these types of compounds. Hence, vapour transport method is used for the growth of single crystals of GeSePb$_x$ (DVT) ($x = 0, 0.1, 0.2, 0.3, 0.4$).

The preparation of single crystals from the vapour phase has been described in many articles [49, 50]. The brief description of this process adopted in the present work is given below.
2.2.1 Growth from Vapour Transport Technique

Vapour growth method is mostly preferred for the growth of layered single crystals as well as for the fabrication of thin layers of metals, insulators and semiconductor type materials. It is convenient for large scale operations i.e. from coating of turbine blades to grow epitaxial layers of semiconductor materials.

In this technique, the materials from which the crystals are to be grown are transported to the growth Zone, kept at comparatively lower temperatures from the source zone which is kept at comparatively high temperature in the form of volatile compounds, which reacts or decomposes to give the material in crystal form and a by-product.

This class of technique can be broadly classified into three categories.

1. Sublimation
2. The Chemical Vapour Transport (CVT) technique and
3. The Direct Vapour Transport (DVT) technique.

2.2.1.1 Sublimation

This method is carried out in either a static or in a floating gas system. In a static system, the material is sealed in a tube and placed in a furnace with thermal gradient. The sublimation takes place in hotter portion of the furnace and the crystal growth in the colder portion. In a float system, an inert gas is passed through the tube over the material in the hot zone, carrying the gaseous species into the colder zone where it deposits. Crystals grown in this manner are of extremely high purity. The method may be applicable to a material that has reasonably high vapour pressure at temperature up to 1000 °C.

2.2.1.2 Chemical Vapour Transport Technique

Several compounds which are not accessible by usual crystal growing methods such as Czochralski or Bridgmann – Stockbarger techniques can be prepared by this method. It is particularly suited for high melting point compounds or for those which decompose without melting. Application of this technique stems on the growth of metal single crystals in halogen atmosphere. This process occurs through chemical reactions in which a solid phase reacts with a transporting agent like iodine, bromine,
NH₄Cl etc. at the source zone to form vapour phase products. In this technique, the temperature gradient is maintained in a multiple zone furnace for the transport of material from source zone to the growth zone of the encasing tube. Proper growth conditions at the growth zone would lead to the growth of the crystals. A large no of layered compounds have been grown by this technique [49-62]. There are various theoretical attempts available in literature [63-68] which have shown that it is possible to grow crystals up to several centimetres in size using this technique under well controlled nucleation condition [63].

CVT technique mainly relies on a chemical reaction between the source material to be crystallized and transporting agent. The reaction product is volatile and can be transported in the vapour phase at temperature well below the melting point of the compound. Transportation occurs between two zones having different temperatures. Usually the starting reaction occurs at a higher temperature and is reversed at the low temperature to deposit molecules of the compound at the most favourable crystalline sites. Initially random deposition occurs until seed crystals are formed. Thereafter growth preferentially occurs on these seeds and large single crystals are formed.

The transportation of the reaction product in the vapour phase can be obtained by a continuous gas flow from external supplies (as in the case of open tube CVT technique) or by its recirculation within a closed tubular ampoule (as in case of the close tube CVT technique). The Process is depicted in Figure 2.2.

In principle, one can transport unlimited amount of starting material with a small amount of transporting agent (just in ideal condition). The rate of transport of compound in gm/cc is given as [54].

\[
M = Ldp (T', T'', Dg, Ct)
\]  

(2.1)

where, \(T'\) and \(T''\) are the temperature at hot end and cold end respectively which should be within stability range of the required crystal type. \(T'\) and \(T''\) depend strongly on the temperature gradient along the ampoule and to a lesser extent on the absolute temperature.
(T’ – T”) is the temperature difference that controls \( dp \), and so used to vary the vapour transport rate. However, this cannot be increased indefinitely without causing polycrystallization [68] as explained below:

Molecules considering on to a flat surface from the vapour lose potential energy, i.e. they acquire binding energy \( E' \). However, their thermal energy gives them a probability, \( p' \) of evaporation as

\[
p' \propto \exp(E'/kT)
\]

\( dp \) is the difference between partial pressure of the reaction product at temperature \( T' \) and \( T'' \). \( Ct \) is concentration of the transporting agent in equation 2.1. A value of 5 mg/cc for \( C_t \) has been found to be good starting point for experiment [54].

L is conductance of the system, which is a function of the ampoule geometry and the physical processes involved in the vapour transport. The conductance of the system depends on the mode of transport of the reaction product. This is controlled principally by the total vapour pressure inside the ampoule, most of which is due to the volatile transporting agent. \( dG \) is the change in Gibb’s free energy in the reaction. It has been found that optimum transport occurs when the reaction is not far from equilibrium, i.e. \( dp \) is maximum for values of \( dG \) not far from zero [52].

For chalcogenides, the halogens are most commonly used as transporting agents, since their \( dG \) values are quit low.

There are three possible mechanisms:

- Diffusion mechanism when the pressure inside the closed ampoule is low and the dimensions of the ampoule are small.
- Convection currents set up due to the thermal gradient when the pressures as well as the dimensions of the ampoule are large.
- Laminar floe of the reaction products take place due to pressure gradient along the ampoule if there is equal number of molecules in the vapour phase on each side of the ampoule.

These results in a reaction like,

- Compound + Transporting agent = Reaction Product.
Figure 2.2: Illustration of the cyclic process of chemical vapour transport in a closed system.

There are usually equal numbers of molecules in the vapour phase each side. If this is not so, there will be a pressure gradient along the ampoule and a laminar flow of the reaction product will take place.

The rate of condensation, \( n \) (mol/sec/cm\(^2\)) is controlled by the partial pressure of the vapour \( P \) (atm) and average molecular velocity \( V \) (cm/sec).

\[
n = L_0 \, P \, V \quad \text{(2.3)}
\]

where \( L_0 \) is the Loschmidt’s constant = \( 2.687 \times 10^{19} \) mole/cm\(^3\) atm.
There will be a pressure, $P'$, where the rate of condensation and evaporation are equal. In reality, when a molecule condenses on crystal. It will tend to migrate over the surface before evaporation. If whilst migrating, it finds a site of greater binding energy $E''$, such as a kink or step on the crystal surface, the probability of evaporation drops. Equilibrium in such cases will occur at pressure, $P''$.

If the partial pressure has a value between $P'$ and $P''$, molecules will only condensed on the site of greater binding energy, $E''$. Under this condition, crystals that have already formed will grow but no new crystals will form unless impurities bind some molecules more firmly to the ampoule wall to form a seed crystal.

Since the net number of molecules condensing is limited by the number of growth sites, the rate of transport must not be too high. Otherwise, the partial pressure of the reaction product will exceed $P'$ and polycrystallization will occur.

Finally, after detailed analysis of transport reaction Nitsche [55] has given the following points for successful growth of material in crystal from using vapour transport technique.

- The rate of transport must not exceed the rate of growth of the seeds.
- The optimum crystallization temperature must be evaluated empirically for each system taking into account the possibility of polymorphism.
- The crystallization chamber should be large in order to prevent intergrowth between adjacent seeds. Asymmetric heating is sometimes useful.
- The temperature distribution in the crystallization chamber should be uniform to avoid partial re-evaporation of already grown crystals.
- Well developed crystals can be formed more easily in large diameter tubes, where transporters convection determines the rate of transport.
- The temperature gradient between two zones must be small when the diameter of the tubes is more. This ensures the even distribution of growth products along the tube. This is because of vapour flow is the rate determining factor.

In this technique, the disadvantage is that the transporting agent may get incorporated as impurities in the crystals during the growth process. So the electrical and thermal properties of the grown crystals get affected up to a certain extent.
2.2.1.3 Direct Vapour Transport Technique

A better method to obtain pure crystals is the direct vapour transport technique, where in the transport of material takes place directly from the source zone to the growth zone due to the temperature gradient set across the encasing tube without using any transporting agent.

A. A. Al. Hilli and B. L. Evans [69] have shown the utility of this method by successfully growing good quality single crystals of some transition metal dichalcogenides. Detailed study of transport reactions occurring during the growth process have been carried out by H. Shafer [69]. The reaction taking place to form AB compound can be given as,

\[ A(s) + B(g) \xrightarrow{T} A(g) + B(s) \xrightarrow{T} AB(g) \xrightarrow{T} A(s) + B(g) \xrightarrow{T} AB(g) \]

One of the elements has lower melting point. So it goes in to vapour form at lower temperatures. This vapour reacts with the other elements at high temperature forming the compound. The same principle has been used to grow the transition metal dichalcogenides using a direct vapour transport technique. In present investigations, GeSePb_x (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4) crystals have been grown using the same technique.

2.3 CHOICE OF THE GROWTH TECHNIQUE

The majority of compounds of the transition metal dichalcogenides belonging to MX_2 group are insoluble in water and decompose before their melting points are reached. Therefore, the growth of such crystals from the melt and aqueous solution is not possible and hence the growth of single crystals of these compounds, using vapour phase technique was found to be most suitable.

The layered crystals grown by the CVT method usually contain small amounts of the transporting agent (e.g. Iodine, Bromine), which may remain as an active impurity and affect the measured properties up to a certain extent. It has been reported that the better method to obtain pure crystals is the direct vapour transport technique and it is possible to grow fairly large crystals of TMDCs by DVT [67] where the transport of materials takes place directly due to the temperature gradient set up across the charge containing ampoule without any transporting agents. Since the
direct vapour transport technique seems to be a better, easier and comparatively an economical method for the growth of pure crystals, this method has been used for the growth of GeSePb_x (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4) crystals in the present work.

2.4 REQUISITES FOR THE DIRECT VAPOUR TRANSPORT GROWTH

In this technique, the materials in their elemental form, from which the crystals are to be grown, are transported from the source zone, which is kept at comparatively higher temperature to the growth zone. During the growth process, the compounds in the volatile form react or decompose to give the material in crystal form. This can be accomplished only if certain requirements of the growth mechanism through this technique concerning the encasing tube as well as the furnace constructions are satisfied. The requirements of the growth process by the direct vapour transport method are given below.

1. Since the technique involves the transport of materials in the vapour form from one region to the other within the enclosed tube placed inside the furnace, it is necessary that the furnace should essentially have two different zones of temperature with proper temperature gradient between them.

2. Since the material is transported in this technique is in vapour form, the encasing assembly should be vacuum-sealed. This would provide an impurity free environment for the growth of crystals to ensure the purity of the grown crystal.

3. The material used to make the encasing assembly should sustain high temperature above 1000°C (which is essentially higher compared to the melting / boiling point of the material to be grown) and at the same time it should not react with the vapour or get corroded by the vapour.

4. Since the temperatures of the two different zones of the furnace are different, it is necessary that they should be independently controlled using two different temperature controllers.

Considering the above requirements a two-zone furnace has to be constructed using windings of a material which can withstand temperatures up to 1200°C. Also, the encasing tube should be of the material which does not melt at high temperatures.
and it should be non-reactive at these temperatures in order to avoid contamination of the grown crystals. Under these circumstances, quartz was considered as the best choice for making the encasing tube.

The following sections cover the furnace design as well as the fabrication of the encasing assembly as per the above requirements.

2.5 DUAL ZONE HORIZONTAL FURNACE

The furnace is the most important part of the present research work to grow the crystals of dichalcogenides. Two – zone furnace provides an appropriate temperature gradient over the entire ampoule. Normally the temperatures employed are fairly high. The temperature gradient within the furnace is required over a length of about 25 cm. Stability of temperature plays an important role, therefore, for this purpose electronic temperature controllers were used.

The furnace was constructed in our University Science and Instrumentation center (USIC) by using special sillimanite threaded tube of grade KR 80 GA HG. This muffle tube is closed at one end and has 500 mm in length, 70 mm outer diameter, 56 mm inner diameter with threaded pitch of 3 mm (Koppers Fabriken Feuerfester, Germany). Super Kanthal A-1 wire of 17 SWG was wound directly on the furnace tube into two different zones or regions. These wires can withstand temperatures up to 1400°C. The tube (Muffle) was enclosed in the glass wool jacket, hot face insulating brick slabs constructed locally and the brick shell was fully enclosed in thick asbestos sheets, and this entire assembly was supported in a steel framework. This arrangement is shown in Figure 2.3. The power supplied to the furnace windings was regulated by the control circuit shown in Figure 2.4. The two regions of windings were provided with independent power supplies and temperature controllers. Transformers with 70V, 80V and 100V taps with 20A current capacity in secondary windings were used to supply sufficient power in order to achieve the required higher temperature.

2.6 AMPOULE PREPARATION

Quartz is considered as the best choice for making the encasing tube. High quality fused quartz tubes of various diameters, having a melting point of about 1500°C were used for growth of crystals. Tubes having internal diameter 22 mm, outer diameter 25 mm and length 250 mm were found to be more suitable. One end of
the ampoule was sealed and the other end was drawn into a neck and joined to another
8 mm inner, 2 mm thickness and 10 mm outer diameter glass tube to connect it to the
vacuum system for evacuation after introducing the source materials. Such a quartz
tube and an ampoule generally used for the crystal growth are shown in Figure 2.5.

Figure 2.3: The dual zone horizontal furnace with axially loaded ampoule.

Figure 2.4: Schematic diagram of complete furnace structure with temperature
controlling system.
Figure 2.5: A quartz tube and an ampoule used for crystal growth.

2.7 CLEANING PROCESS OF AMPOULES

Cleaning of ampoule is an important step in the crystal growth process. The ampoule was first washed with boiled water along with a suitable detergent, after that it was washed with a hot mixture of concentrated HNO$_3$ and HF (49%) taken in equal proportion. Then the washing was followed by double distilled water. Again it was washed with a mixture of concentrated HNO$_3$ and H$_2$SO$_4$ taken in equal volume. Ampoule was then filled with concentrated HF and heated at 70$^\circ$C temperature for about half an hour in order to make the inner surface of ampoule slightly rough which is useful for the better growth of crystals. Finally washing was done by double distilled water for 8 to 10 times. Then the clean ampoule was transferred into the oven kept at 100$^\circ$C temperature and left overnight to make it moisture free.

2.8 SEALING OF AMPOULES

For the crystal growth of GeSePb$_x$ (DVT) ($x = 0, 0.1, 0.2, 0.3, 0.4$), the required materials shown in the Table 2.1, were taken in a stoichiometric proportion using the “AFCOSET” electronic weighing machine and filled up in a transparent ampoule duly cleaned and dried by the process explained above. A total amount of constituent materials used was 10 gm in each experiment. The ampoule containing the source material was then connected to a vacuum system. The ampoule was sealed at a pressure of about $10^{-5}$ torr. In this process, proper precaution was taken for slow vacuum, so that materials from the ampoule could not enter into the vacuum system.
and the proportion of the constituent elements remains constant. The sealed ampoule was shaken thoroughly for proper mixing of the constituent materials.

Table 2.1: Selected materials for crystal growth

<table>
<thead>
<tr>
<th>Material</th>
<th>Purity</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Germanium</td>
<td>99.99%</td>
<td>Alfa Aesar, U.K.</td>
</tr>
<tr>
<td>Selenium</td>
<td>99.99%</td>
<td>Alfa Aesar, U.K.</td>
</tr>
<tr>
<td>Lead</td>
<td>99.99%</td>
<td>Alfa Aesar, U.K.</td>
</tr>
</tbody>
</table>

2.9 GROWTH OF GeSePbx (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4) SINGLE CRYSTALS

The sealed ampoule containing stoichiometric mixture of required materials was loaded in the two zone horizontal furnace and the temperatures of both the zones were raised slowly for reaction between elements. The temperatures and the period for which the ampoule was kept in the furnace depended upon the material, which was being grown. A slow heating was necessary to avoid any possibility of explosion due to the strong exothermic reaction between the elements. After some stipulated time of keeping the ampoule at elevated temperatures, a slow cooling process was carried. The rate of cooling should be as slow as possible for enhancing the nucleation and growth process. The typical temperature profile of the growth run of grown crystals is shown in Figure 2.6.

Figure 2.6: The temperature profile used for the growth of GeSe (DVT).
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The growth parameters of grown crystals such as temperature distribution, growths period etc. used for the growth of different materials have been given in Table 2.2.

**Table 2.2:** Growth parameters for grown crystals.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Temperature Distribution(^{0}\text{K})</th>
<th>Growth Period (Days)</th>
<th>Dimensions of Grown Crystals (cm (\times) cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeSe</td>
<td>903 Reaction Zone, 853 Growth Zone</td>
<td>7</td>
<td>0.8 (\times) 0.7</td>
</tr>
<tr>
<td>GeSePb\textsubscript{0.1}</td>
<td>875 Reaction Zone, 845 Growth Zone</td>
<td>7</td>
<td>0.8 (\times) 0.9</td>
</tr>
<tr>
<td>GeSePb\textsubscript{0.2}</td>
<td>885 Reaction Zone, 835 Growth Zone</td>
<td>7</td>
<td>0.9 (\times) 0.6</td>
</tr>
<tr>
<td>GeSePb\textsubscript{0.3}</td>
<td>890 Reaction Zone, 825 Growth Zone</td>
<td>7</td>
<td>0.9 (\times) 0.7</td>
</tr>
<tr>
<td>GeSePb\textsubscript{0.4}</td>
<td>895 Reaction Zone, 805 Growth Zone</td>
<td>7</td>
<td>0.7 (\times) 0.5</td>
</tr>
</tbody>
</table>

The growth of any compound in crystal form depends upon various parameters such as the length of the ampoule, purity of the source materials used, quality of the quartz tube, level of vacuum, amount and type of transporting agent, temperature distribution of the furnace, appropriate proportion of constituent element, time duration for growth cycle, the rate of increase and decrease of temperature etc.

The temperature was increased at the rate of 40\(^{0}\text{C}\) /hr, till it attained the required temperature in both zones. For the growth of GeSePb\textsubscript{x} (DVT) (x = 0, 0.1 ,0.2, 0.3, 0.4), the ampoule was left in the furnace for 7 days after that temperature was decreased at the rate of 20\(^{0}\text{C}\) /hr till the room temperature. After this furnace was switched off. The ampoule was carefully taken out of the furnace. It was seen that at the growth zone for all above mentioned crystals, the ampoules contained gray, shiny irregular shaped platelets of crystals. The grown crystals were carefully taken out by breaking the ampoule.

**2.10 RESULTS AND DISCUSSION**

The crystals of GeSePb\textsubscript{x} (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4) compound have been successfully grown using direct vapour transport technique. The photographs of the ‘as grown’ crystals of GeSePb\textsubscript{x} (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4) are shown in Figure 2.7. The dimensions of grown crystals have been shown in Table 2.2. The grown
crystals have been found enough large in dimensions. It is found that GeSePb\textsubscript{x} (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4) compounds grow in the form of thin platelets.

\textbf{Figure 2.7}: As grown single crystals of GeSePb\textsubscript{x} (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4).

\textbf{2.11 CONCLUSION}

1. It is possible to grow single crystals of GeSePb\textsubscript{x} (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4) by direct vapour transport technique.

2. Single crystals of GeSePb\textsubscript{x} (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4) were found to grow in the form of thin platelets showing a mirror like metallic luster.

3. Growth conditions and growth mechanism for the growth of large size GeSePb\textsubscript{x} (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4) single crystals have been determined by trial and error method.
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REFERENCES

Chapter - 2: Growth of GeSePb_x (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4) Single Crystals


[34] F. Stober, Z. Krist, 61 (1925) 299.


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