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THE GROWTH OF TERNARY SEMICONDUCTOR CRYSTALS
SUITABLE FOR DEVICE APPLICATIONS

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Abstract. — In general, the growth of I-III-VI$_2$ and II-IV-V$_2$ chalcopyrite-type crystals of suitable quality for device applications has been difficult. In some cases, the problem lies in not being able to produce large single crystal specimens, while in others the quality of the crystal is not adequate for the purposes intended. Techniques for both material synthesis and crystal growth of chalcopyrite compounds will be discussed along with factors which lead to the formation of growth defects. Examples from recent experiments on the growth of three important non-linear optical materials, CdGeAs$_2$, AgGaSe$_2$, and AgGaS$_2$, will be given.

1. Introduction. — A number of ternary compounds, particularly those of the I-III-VI$_2$ and II-IV-V$_2$ types having the chalcopyrite crystal structure, are currently of interest for optical and semiconductor applications [1, 2]. Although a variety of growth techniques, including Bridgman-Stockbarger, gradient freeze, zone leveling, chemical vapor transport, solution, and liquid encapsulated Czochralski growth have been used to grow these materials, most crystals reported in the literature contain one or more of the following defects: (1) polycrystalline regions, (2) cracks, (3) compositional inhomogeneities, (4) precipitates, (5) twins, (6) striations, and (7) gaseous inclusions and voids. Of the thirty-six chalcopyrite compounds which have been synthesized to date, there is no way to a priori assess the ease with which they can be grown in single crystal form suitable for device applications. Some are relatively straightforward to grow and others extremely difficult.

Some factors which make the chalcopyrite compounds difficult to grow are: (1) three different elements have to find an appropriate site on the growth interface, (2) the ordered superlattice structure leads to a greater chance for point defects, (3) a large thermal expansion anisotropy exists in many members of the chalcopyrite family which is related to the uniaxial tetragonal distortion along the c-axis, (4) adequate ternary phase equilibria information is rarely available, (5) many compounds do not melt congruently, (6) some of the constituent elements have a high vapor pressure, and compounds a significant dissociation pressure, and (7) most of the compounds appear to have moderately low fracture strengths.

The demand for large, high quality crystals of several of these compounds has prompted extensive investigations aimed at identifying the type and origin of the various defects which can occur in these crystals, and in developing techniques to control or eliminate them. Many of these studies included experiments designed to gain a more thorough understanding of phase equilibria, nucleation and growth mechanisms, thermal stress factors, reactivity of system components, and the physical properties of the compounds and their melts.

Single crystals of three important ternary semiconductors having the chalcopyrite structure, CdGeAs$_2$, AgGaSe$_2$, and AgGaS$_2$ together exhibit almost all of the defects described. As a consequence, it has proven very difficult to grow suitable crystals of these materials for optical applications. Some of the properties of these materials are given in table I. Note the large thermal expansion anisotropy of these compounds as well as their large non-linearity and birefringence. Experiments designed to improve the quality of these crystals will be described. Included will be a discussion of the growth of CdGeAs$_2$ crystals from both pure melts and Bi solutions [3]. Various crystal characteristics; morphology, structural integrity, inclusions, twinning, and optical transparency, will be discussed as a function of growth conditions. Also to be described will be the preparation of large antwinned AgGaS$_2$ and AgGaSe$_2$.
son properties of three chalcopyrites useful for non-linear optics

<table>
<thead>
<tr>
<th>Property</th>
<th>AgGaS₂</th>
<th>AgGaSe₂</th>
<th>CdGeAs₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>42 m</td>
<td>42 m</td>
<td>42 m</td>
</tr>
<tr>
<td>a</td>
<td>5.755 Å</td>
<td>5.985 Å</td>
<td>5.943 Å</td>
</tr>
<tr>
<td>(2 - \frac{c}{a})</td>
<td>0.218</td>
<td>0.183</td>
<td>0.110</td>
</tr>
<tr>
<td>Melting point</td>
<td>970 °C</td>
<td>850 °C</td>
<td>670 °C</td>
</tr>
<tr>
<td>Thermal expansion ((\alpha_2/\alpha_{11}))</td>
<td>(-2 \times 10^{-5} ^\circ C^{-1})</td>
<td>(+2.5 \times 10^{-5} ^\circ C^{-1})</td>
<td>(+8.5 \times 10^{-6} ^\circ C^{-1})</td>
</tr>
<tr>
<td>Electrical band gap</td>
<td>2.7 eV</td>
<td>1.7 eV</td>
<td>0.53 eV</td>
</tr>
<tr>
<td>Transparency range</td>
<td>0.5-13 μm</td>
<td>0.7-18 μm</td>
<td>2.3-18 μm</td>
</tr>
<tr>
<td>Birefringence ((E &lt; E_g/E &lt; E_g))</td>
<td>-0.055</td>
<td>-0.033</td>
<td>+0.157</td>
</tr>
<tr>
<td>Non-linear optical coeff. ((d_{35}/d_{36}(GaAs)))</td>
<td>0.13</td>
<td>0.37</td>
<td>2.6</td>
</tr>
</tbody>
</table>

2. Material synthesis. — There are a number of methods which have been utilized for the synthesis of chalcopyrite compounds:

(a) Direct fusion of the elements

ex. Cd + Ge + 2 As → CdGeAs₂.

(b) Reaction of binary compounds (fusion or sintering)

ex. Ag₂S + Ga₂S₃ → 2 AgGaS₂.

(c) Reaction of an element with a binary compound or alloy (fusion, sintering or vapor phase reaction)

ex. Ge + CdAs₂ → CdGeAs₂

ex. 2 S₄(1) + (AgGa)(1) → AgGaS₂(1).

(d) Synthesis in other media (useful where the compound dissociation pressure is high)

1. solution,

2. gas phase reactions.

To avoid reactions with oxygen, all are synthesized in evacuated quartz ampoules which are sometimes back-filled with an inert gas.

Choice of the most suitable technique to employ depends upon (1) reaction temperature of constituents and melting temperature of the compounds, (2) vapor pressures of the elements, (3) dissociation pressure of intermediate or final compounds, (4) heat of reaction, (5) reactivity of constituents, and (6) purity and stoichiometry of starting materials available.

Direct fusion of the elements is usually the best choice provided the compound is congruently melting and excessive vapor pressure or chemical reactivity is not a problem. (These factors are not always prohibitive.) This method is desirable because the elements are usually available in a quality superior (with regard to stoichiometry and purity) to most binary compounds obtainable commercially or synthesized in the laboratory, and impurities are usually found in material prepared in other media (liquid or gaseous solutions).

Compounds containing sulfur and phosphorous are more difficult to prepare since the S and P pressure can reach high values while heating mixtures to the reaction temperature. In the literature, many examples of capsule explosions resulting from excessive gas pressures have been reported [7, 8]. Slow heating and double wall capsules have been used to minimize these problems during the direct fusion process.
Figure 1 shows a schematic diagram of an apparatus used for the synthesis of AgGaS₂ by reaction of a molten alloy (Ag-Ga) with S vapor. A sulfur pressure of about 2 atm was maintained over the melt at 1050 °C. The product was generally light yellow in color but did contain a black second phase which x-ray diffraction analysis revealed to be principally AgGaS₂.

Electron microprobe analysis showed that this black phase, however, was rich in silver. This is consistent with the observation that a small amount of Ga₂S₃, which is somewhat volatile, was found condensed on the walls of the quartz reaction chamber. The black material was easily removed from the synthesis product by unidirectional solidification, a technique similar to the growth technique which will be described later.

The products of the preparative techniques will be in one of the following forms:

(a) Stoichiometric and pure (ready for growth).
(b) Non-stoichiometric.
(c) Stoichiometric but incongruently melting (multiphase product).
(d) Containing partially unreacted products.
(e) Containing impurities.

If the material as synthesized is not suitable for growth, as is the case previously described for AgGaS₂, a post-preparation treatment of the product might be desirable such as:

(a) Zone refining.
(b) Unidirectional solidification (pregrowth).
(c) Decanting.
(d) Out-gassing.

The lower vapor pressure of the elements comprising CdGeAs₂ and AgGaSe₂ permit the use of direct fusion in their synthesis. Problems still exist, however, which may be attributed to either a misinterpretation of what little is known about phase equilibria in these three-component systems, or a lack of adequate thermodynamic and crystallization kinetic data.

3. Crystal growth. — Some techniques which have been used for the growth of chalcopyrite crystals are:

(a) Bridgman-Stockbarger, gradient freeze
   — horizontal,
   — vertical.
(b) Solution (flux).
(c) Chemical vapor transport.
(d) Zone leveling.
(e) LEC (liquid encapsulated Czochralski).

Of these, the Bridgman-Stockbarger and gradient freeze techniques have been most widely used. The vertical Bridgman process is preferred from the point of view of thermal symmetry and small surface to volume ratio, while the horizontal technique in many cases allows the convenient use of seeds, and the solid-liquid interface can be observed and its position adjusted. The chemical vapor transport method [9, 10] has yielded cm-sized samples of a wide variety of compounds which might not be obtainable by other techniques. Generally, size is one of its primary limitations. This is true also for solution growth technique which has some added disadvantages (most importantly, inclusions). The zone leveling technique has been applied by Lerner [11] to the growth of several compounds which do not melt congruently.

Some criteria for choosing a suitable growth technique are:

(a) chemical reactivity of compound or constituents with surrounding media,
(b) vapor pressures of constituents and dissociation pressures of compounds at growth temperature,
(c) extent of solid solubility,
(d) whether it melts congruently or incongruently,
(e) size of crystal required,
(f) crystal orientation,
(g) degree of purity (or dopant concentration) required, and
(h) stress-related problems.

Not all of the information on which to base an intelligent decision will be available and so trial and error is often the rule rather than the exception.

The choice of furnace parts compatible with the chalcopyrites is rather limited and usually quartz and carbon (graphite, amorphous, pyrolytic) are widely used for both synthesis and growth processes. Even these commonly used materials are not entirely inert and so caution must be exercised to prevent sample contamination.

CdGeAs₂. — In the author’s laboratory several techniques have been employed in attempts to grow large high quality crystals of CdGeAs₂ including the Bridgman technique (vertical and horizontal), flux growth (unconstrained free crystallization and unidirectional solidification), and some preliminary work on liquid encapsulated Czochralski growth. In the latter case, the melting point of 670 °C is too low for B₂O₃ to be an effective encapsulant and a suitable encapsulant has not yet been found. One difficulty with CdGeAs₂ is that control of both the Cd and As partial pressure over the melt is necessary to maintain stable melt conditions.

In figure 2, a schematic diagram of the standard type Bridgman furnace is shown. This equipment was used for the growth of not only CdGeAs₂, but also AgGaS₂ and AgGaSe₂. The axial temperature gradient can be adjusted over a wide range but typically 40-50 °C/cm was used. In the literature, temperature gradients of from as low as 0.24 °C/cm to 160 °C/cm have been reported. It is not well understood what exact role the temperature gradient does play, except that it is generally believed that establishment of a near-planar interface is most desirable and this can be achieved by adjusting the ΔT. Bridgman melt-growth of CdGeAs₂ proved extremely difficult, with the major problems being (1) secondary nucleation, (2) polycrystallinity, (3) cracking, and (4) poor
transparency. Nucleation problems lead to boules which are not single. Polycrystalline boules crack badly due to the large stresses which develop as a result of the thermal expansion anisotropy of adjacent grains, and cracked samples are usually opaque since the incident light is scattered off grain and crack boundaries. Twins are also found in regions of the boule usually at an angle of 300 to the boule axis. In one boule which grew single, the twin boundary was parallel to the boule axis and suggested that it might be important to have a particular crystallographic orientation parallel to the boule axis. Figure 3 shows a boule which has two grains and clearly illustrates how the cracks are concentrated at the grain boundary and radiate from it across the boule diameter. Even small diameter crystals crack, indicating that thermal stress on cooling is not the primary source of fracturing.

To gain more insight into the problems inherent in growing high quality crystals of CdGeAs₂ from the melt, solution growth techniques were explored [3]. After studying a number of different solvents, Bi was chosen as one of the most appropriate. The binary section Bi-CdGeAs₂ is shown in figure 4. This diagram has two interesting features; one the shallow slope of the liquidus in the CdGeAs₂-rich region and secondly at the high solvent side the existence of a GeAs + L phase field just below the liquidus. In the former region, a large amount of material will come out of solution immediately upon crossing the liquidus making the control of nucleation difficult. At the high solvent side GeAs will be the first phase to crystallize and could again interface with the nucleation and growth of CdGeAs₂ crystals forming at lower temperatures.

In spite of this unfavorable situation, crystals of some promise were grown in both regions, figure 5. The large crystals (top) were formed during free crystallization experiments with high solute solution compositions. These crystals were single, but were cracked because they were attached to a polycrystalline base and also due to the presence of inclusions. The smaller crystals were grown at high solvent compositions co-existent with GeAs crystals. These were the first uncracked crystals of CdGeAs₂ produced. The morphology of these crystals is similar to ZnSiP₂ crystals prepared by the chemical vapor transport process [12] where the fast growth direction is along the [111].

Unfortunately, although having a well-formed morphology with mirror smooth facets, the crystals usually exhibited a cored region containing solidified solvent, figure 6. A longitudinal cross section into...
the core region shows dendritic branching, figure 7. Also found in the smaller crystals were twins parallel to the long crystal dimension and therefore, the [111]. Since the twin found in the good single crystal boule produced from the melt was parallel to the boule axis, this boule must have grown with the fast growth axis nearly parallel to the boule axis. Control of growth orientation may be an important factor if high quality crystals are to be consistently produced.

Attempts to seed the Bridgman runs with [111] oriented seeds proved difficult and controlled growth in this direction has not yet been achieved.

In an effort to produce usable solution-grown crystals a 5.65 % alloy of Cd and As was added to the Bi solution. Elimination of the GeAs + L phase field was achieved, figure 8. Solution growth experiments were performed in an apparatus which allowed variation of temperature gradient, solution composition, and cooling rate, while permitting visual observation of supercooling, nucleation, and growth characteristics. Even under these carefully monitored conditions controlled growth could not be achieved. Inclusions, autonucleation, and primary and secondary nucleation effects were all observed, figure 9. The solidified included solvent containing Cd and As contained small triangular crystals of Cd$_3$As$_2$, figure 7. These are similar to inclusions found in some melt growth material, figure 10.

The use of the Bridgman technique with Bi + CdGeAs$_2$ solutions resulted in large boules of a quality equally as poor as that found in pure melt growth experiments, with the added possibility of inclusions. If the capillary region was tapered to a
Features of early experiments included compositional inhomogeneities along the length of the boule, including inclusions of Ga$_2$Se$_3$ in the capillary region and Ag-rich material at the top of the boule. Also found were surface voids, and some cracking not usually related to polycrystallinity, but possibly an interaction with the crucible used during growth. Differential expansion, surface reaction, and adherence of the crystal to the wall of the crucible, or perhaps thermal stresses on cooling, might be responsible for crystals cracking.

The crystal quality was vastly improved by making the following changes: (1) in situ preparation and growth so that no material is lost in transference from one capsule to another, (2) widening the capillary section to a 4 mm diameter to permit homogenization of the entire melt, (3) use of a heavy pyrolytic carbon coat produced by cracking acetone on the inside walls of the capsule, and (4) the use of slow growth rates (~0.4 mm/day).

The phase diagram for Ag$_2$Se-Ga$_2$Se$_3$ was studied by Platnik and Belova [13] and AgGaSe$_2$ was found to be congruently melting. Our own experiments seemed to confirm [4] this result and so compositional variations were believed due to one or more of the following: (1) imprecision in weighing, (2) loss of components to the vapor state above the melt, and (3) growth kinetics which vary from those used to define the phase diagram. A study was made along the Se-(Ag:Ga) binary section in the Ag-Ga-Se ternary system, figure 12. It shows that Se-deficient compositions have more complicated phase equilibria structure than Se-rich compositions suggesting that the formation of phases other than AgGaSe$_2$ near the
the composition sufficiently so that new phase fields can form under normal growth conditions. One can minimize this effect by (1) reducing the free volume in the capsule above the melt, or (2) sealing the melt, perhaps with a liquid encapsulant.

To eliminate surface voids on AgGaSe₂ and AgGaS₂, a study of bubble formation was carried out. It was observed that bubbles nucleated on the capsule walls and grew in size and number during the first twenty hours after melt down. By leaving the melt at about 200 °C above the melting point for 24 hours and then vibrating the capsule for a short while the bubbles could be easily removed. The higher temperature reduces the viscosity sufficiently to allow the bubbles to float to the surface and break. One possible mechanism which has been suggested for the occurrence of bubbles is the reaction of S and Se in the melt with impurities in the quartz (H₂ or H₂O for example) forming gaseous species, i.e., H₂S or H₂Se. The impurity available for reaction would then be depleted after some period of time and bubble formation and growth would terminate.

The boule, although improved dramatically, still had scattering centers which reduced the optical quality. Absorption losses made the material unsuitable for non-linear applications. The exact nature of the scattering centers was difficult to identify visually. It is thought likely that more than one type of center

![Fig. 12. AgGa-Se alloy binary section.](image)

![Fig. 13. Scattering centers in AgGaSe₂ observed with IR transmission microscopy.](image)
may be present. Figure 13 shows some typical scattering centers observed using IR microscopy.

Phase equilibria information on the Ag-Ga-S ternary system is very limited but its behavior is probably quite similar to the selenide system. The starting material was produced from vapor-synthesized material which had been pre-grown to separate the dark Ag-rich phase from the near stoichiometric yellow material. The maximum allowable growth rate for AgGaS$_2$ was greater than with AgGaSe$_2$ by a factor of 10. A very heavy pyrolytic carbon coating was applied (15-20 individual coatings) on the inner surface of the quartz capsule. The results of this technique are bright yellow crystals with good compositional uniformity, few cracks and twins, but microscopic scattering centers similar to those in AgGaSe$_2$, giving the material a milky translucent appearance. Evacuated and sealed growth capsules did not crack as had been previously reported in the literature.

![Diagram of the pseudo binary Ag$_2$Se-Ga$_2$Se$_3$ phase diagram](image)

**Fig. 15.** Pseudo binary Ag$_2$Se-Ga$_2$Se$_3$ phase diagram after Platnik and Belova [13].

Typical scattering centers found in AgGaS$_2$ are shown in figure 14. They appear elongated and oriented parallel with respect to one another.

4. Reduction in scattering losses. — The Ag$_2$Se-Ga$_2$Se$_3$ binary diagram of Platnik and Belova [13] is given in figure 15. Note that on the Ge$_2$Se$_3$-rich side of the ternary compound lies a wide solid solubility region at high temperature. If the melt were Ga$_2$Se$_3$-rich, then the crystal would also be Ga-rich at high temperature. Upon cooling, the crystal would cross into a two-phase subsolidus region where a second phase could precipitate out. At lower temperatures another two-phase region is traversed and yet another phase could be formed without dissolution or reaction of the first precipitate, depending on kinetic factors. Electron microprobe analysis of some precipitates in AgGaSe$_2$ crystals suggest they are Ag-rich. The melt composition for AgGaS$_2$ growth was, if at all non-stoichiometric, probably slightly Ag-rich as a result of the vapor synthesis process. This is inconsistent with what would be expected from Ag$_2$Se-rich melt compositions in the plane of the pseudo binary Ag$_2$Se-Ga$_2$Se$_3$ phase diagram. It is most likely, therefore, that the cause of precipitation in these materials is related to a high temperature solid solution region not represented in this binary section, but in another compositional plane of the ternary system. If this is true, it should be possible, therefore, to quench from within the solid solution region at high temperature to obtain a precipitate-free, metastable solid solution.

Quenching experiments on both selenide and sulfide crystals gave confirming results [6]. With quench rates of up to 23°C/s, optical scattering in bulk materials was drastically reduced.

Figures 16 and 17 show improved transmission microphotographs of quenched and unquenched samples of AgGaSe$_2$ and AgGaS$_2$, respectively, clearly demonstrating the elimination of most visible scattering defects. In figure 18, a macrophotograph shows the dramatic improvement in optical quality of AgGaS$_2$ and figures 19 and 20 show the improvement in spectral transmission over the entire transparency range of AgGaSe$_2$ and AgGaS$_2$.  

![Figure 14: Optical transmission photomicrograph of scattering centers in AgGaS$_2$](image)

**Fig. 14.** Optical transmission photomicrograph of scattering centers in AgGaS$_2$. 

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*References*

1. Platnik, G. and Belova, V. Composition and structural properties of AgGaS$_2$ and AgGaSe$_2$. *J. Appl. Phys.* 60, 4154-4160 (1986).


FIG. 16. — IR transmission photomicrograph, (a) before and (b) after quenching AgGaS$_2$.

Fig. 17. — Optical transmission photomicrograph, (a) before and (b) after quenching AgGaS$_2$.

Fig. 18. — Macrophotograph of two AgGaS$_2$ crystals (top) unquenched, (bottom) quenched.
5. Conclusion. — The chalcopyrites have proven a great challenge to investigators attempting to reproducibly prepare crystals suitable for device applications. Relevant information important to understanding nucleation and growth behavior is slowly being generated and like a difficult jigsaw puzzle eventually the pieces will fall into place, and material suitable for technological applications will finally become available.

References