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TECHNICAL OPERATIONS SUPPORT (TOPS) III
Delivery Order 0007: Chalcopyrite Crystal Growth

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Fisk University

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Final Report

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14. ABSTRACT
1. Chalcopyrite crystal growth - AgGaSeTe was grown via Accelerated Crucible Rotation Technique (ACRT). ACRT did provide good homogeneity and elimination of bulk bubbles, however overall crystal quality was inferior to crystals grown by Horizontal Bridgman technique. The anisotropic expansion of AgGaSeTe results in better growth in horizontal configurations which leave a degree of freedom for expansion and contraction along the long, unrestricted (top) side of the crystal. AgGaSe2 and AgGa0.6In0.4Se2 was grown using horizontal Bridgman. Characterization via photoluminescence, optical transmission, and Raman indicate high crystal quality.

2. LiGaX2 crystal growth - LiGaTe2 and LiGaSe2 were grown using horizontal electrodynamic gradient technique with a 24-zone furnace. Li could not be obtained with purity better than 99.99%. Synthesis and crystal growth were done in the same carbon-coated vessel, in order to accommodate the high reactivity of Li with the ampoule walls and with air.
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14. ABSTRACT, concluded

The LiGaTe2 crystal was of good optical quality for a first attempt at this material, however only a small single crystal could be mined from the polycrystalline ingot that resulted from the growth attempt. A larger crystal was obtained from the LiGaSe2 growth, but its optical quality was very poor.

3. GaTe crystal growth - GaTe, GaSe0.2Te0.8, GaSe0.8Te0.2, and GaSe were grown via vertical seeded Bridgman, resulting in large crystals of good quality. Optical band gaps were measured by optical transmission and photoluminescence. These results are encouraging that further work could result in a ternary crystal with improved terahertz nonlinear optical performance over GaSe.

Final Technical Report for the TOPS III efforts on growth of crystals for infrared applications

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I) Chalcopyrite Crystal Growth ($80k)

1) Setting up an Accelerated Crucible Rotation Technique (ACRT) and AgGaSeTe
For the growth of nonlinear optical material AgGaSeTe (AGST) was investigated for frequency-doubling the output of CO_2 lasers into mid-infrared spectral range.

-
- The accomplishments in this project were:
  - a) material synthesis procedure. Stoichiometric charge of elements was sealed under vacuum of 1.5×10-7 torr. Heated up to 800 0C at a rate of 60/hr, soaked for 18 hrs. Ampule was kept at ~450 and rotated at 20 rpm. Cooldown at a rate of 60/hr
  - b) Efficient mixing can achieved through the use of Accelerated Crucible Rotation Technique (ACRT) shown in Figure 1, whereby the molten charge is rotated back and forth in manner similar to that of a washing machine. The effectiveness of ACRT is strongly affected by the interaction of rotational forces with buoyant forces. Our assumption is that a better homogeneity of the liquid composition can be achieved resulting in a better uniformity of the grown crystals. [Ref: H. J. Scheel, Accelerated crucible rotation: A novel stirring technique in high temperature solution growth, Journal of Crystal Growth, Volumes 13-14, May 1972, Pages 560-565] Crystal growth was attempted however due

to the vertical configuration inherent to this technique the crystals were inferior to the ones grown by us from the same starting materials and using a parallel system at Fisk in horizontal configuration. We explain these results as being caused by the anisotropic behavior of the thermal expansion of the crystals being more confined to the crucible walls in the vertical geometry. Good mixing was obtained by ACRT by changing the direction of rotation and resulting in bulk bubble elimination. However bubbles still existed on the surface of the ingot, next to the fused silica wall. Unfortunately, the vertical geometry of ACRT is also less amenable to seeding.

- We have successfully grown single crystals of $AgGaSe_2$ and $AgGa_{1-x}In_xSe_2$ (x= 0.1-0.3) quaternary crystals using horizontal Bridgman technique. The synthesis of $AgGa_{0.6}In_{0.4}Se_2$ has been completed and the crystal growth is underway. The synthesis and growth of the crystals were carried out at 850-900^0 C using elemental Ag, Ga, In. and Se. The stoichiometry of the grown crystals was evaluated using EDAX measurements. The grown AGS and quaternary crystals were fully characterized by Photoluminescence, optical transmission and Raman spectroscope along the growth direction and cross-sections.

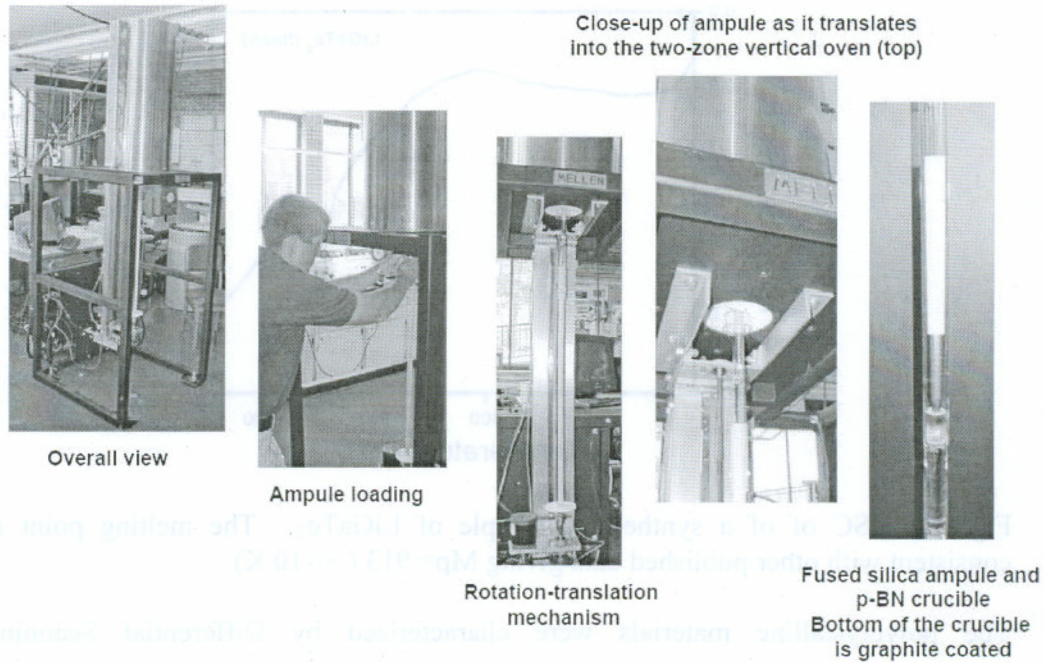

Figure 1. ACRT system at Fisk.

II) $LiGaX_2$ Crystal Growth (\$50k)

Recently, growth of the noncentrosymmetric, chalcopyrite structure crystals of Li based nonlinear crystals such as $LiGaTe_2$ and $LiGaSe_2$ has attracted much attention due to several remarkable nonlinear properties. Synthesis and growth of $LiGaSe_2$ and $LiGaTe_2$ was carried out in glassy carbon crucible around 600-650^{0}C by electrodynamic gradient technique (EDG) using 24-Zone furnaces. Polycrystalline with small grain crystal was obtained. The purity of Li is at best of 99.99% and it is regarded as the major impediment in realizing higher quality optical material.
Both synthesis and growth are carried out in carbon glassy crucible without breaking the vacuum due to high chemical reactivity of Li containing compound with fused silica tube.

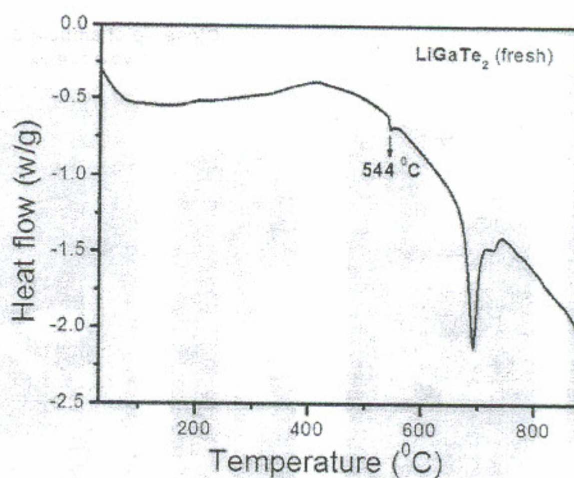

Fig. 2. DSC of of a synthesized sample of $LiGaTe_2$. The melting point is consistent with other published data giving Mp= 913 (+/-10 K)

The polycrystalline materials were characterized by Differential Scanning calorimetry (DSC) shown in Fig 2. Alumina crucible was used in the temperature range from room temperature to 900 °C at 1 atm. of flowing dry nitrogen.

A $LiGaSe_2$ ingot and wafers are shown in Figure 3. The temperature gradient was 10 ^{0}C/cm and the temperature profile moved to obtain a growth rate of 0.5 cm/day.

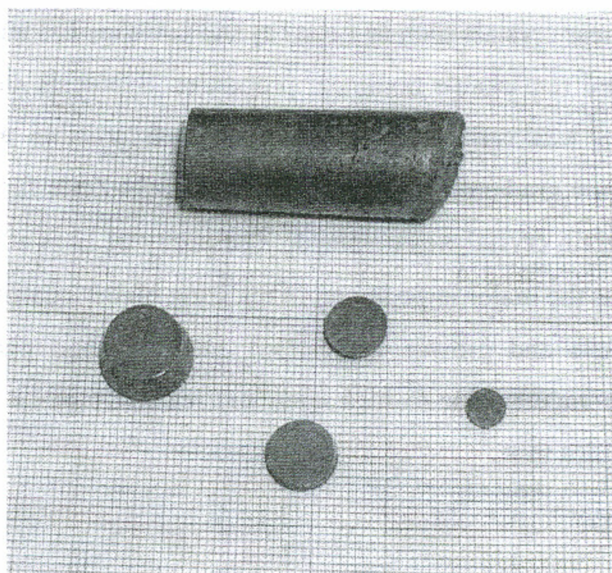

Fig. 3. Ingot and wafers of $LiGaSe_2$ grown in this project.

In the $LiGaTe_2$ system, we have obtained small grain polycrystalline LGT crystals. Isenko et al. [I. Isaenko, P. Krinitsin, V. Vedenyapin, A. Yelisseyev, A. Merkulov, J. J. Zondy and V. Petrov. Crystal Growth and Design, 5,1325 (2005). also. I. Isaenko, I. Vasilyeva, A. Merkulov A. Yelisseyeva, S. Lobanov, J. of Crystal Growth, 275, 217 (2005).] reported that they used Ar overpressure to prevent the dissociation of $LiGaTe_2$ during Bridgman growth. The high reactivity of Li with ampoules and air along with low purity may prevent for obtaining large single crystal (larger than the one shown in Figure 4) for LGT. We could obtain larger crystals of $LiGaSe_2$ however their optical transparency was quite poor.

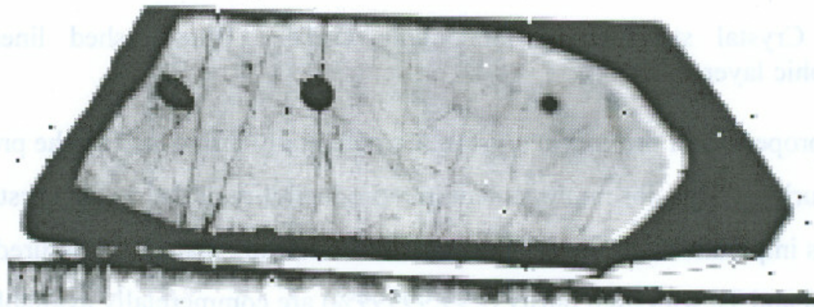

Fig. 4 Near-IR photo of a $LiGaTe_2$ crystal (3mm X1.5 mm)

III) GaTe Crystal Growth (\$35k)

- GaTe has a centrosymmetric monoclinic crystalline structure that is arranged into planes, shown in Fig. 5, where van der Waals bonds occur between the Te terminated planes. There are both Ga-Te and Ga-Ga bonds within the planes of GaTe. Ga vacancies have been suggested to give rise to a shallow acceptor level at 0.15-0.18 eV above the valence band, which causes the material to be exclusively p-type. GaTe is a stable compound, melts congruently and has no solid-state transitions [Yves Feutelais, Bernard Legendre, "Binary phase diagrams of tellurium and post-transitional elements (IB, IIB, IIIB, IVB, VB, VIB)" Thermochimica Acta 314 (1998) 35-53]

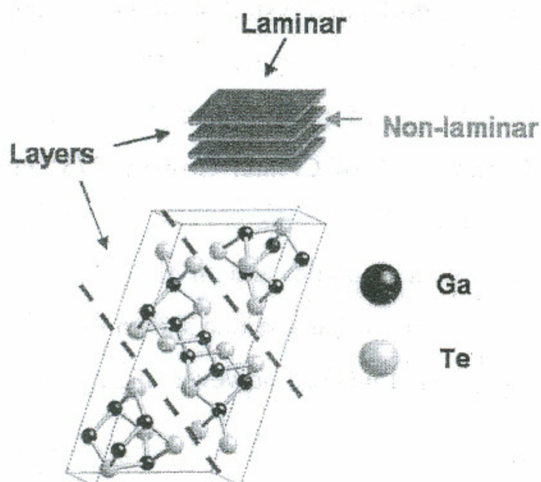

Fig. 5. Crystal structure of monoclinic GaTe. Blue dashed lines indicate crystallographic layers.

The optical properties of the grown crystals are potentially influenced by the presence of residual impurities. Thus for improvement in reproducibility of the grown crystal qualities, it is imperative that the purity (>6N) of the starting material is assured. Elemental Ga and Te with high purity (>99.99999%) are commercially available. GaTe crystals were grown using stoichiometric amounts of high purity (7N) Ga and 7N zone refined Te as starting materials to make a homogeneous polycrystalline ingot.
The synthesis was carried out at 900 oC (melting point was determined to be 826 °C using Differential Scanning Calorimetry) for 12 h. The charge was slowly heated at a rate of 0.4 °C/min in tubular resistance heated furnace. The charge materials are continuously rotated for uniform mixing. at an angle of ~ 45° with constant rotation of the ampoule ~ 20 rpm. After complete synthesis, the ampoule was cooled to room temperature. One of the undoped crystals obtained is shown in Figure 6.

The polycrystalline ingot was then placed in a conically tipped thick-walled (≥3 mm) carbon coated quartz ampoule and sealed under a vacuum of 10^{-6} torr. The conical tip was specially designed to initiate and hold a GaTe seed crystal, which prevents secondary nucleation and allow growth along a preferred orientation. An axial low temperature gradient (~ 10°C/cm at the growth zone) was imposed by tuning the input power

distribution into the heater to stabilize the solid-liquid interface. The sealed ampoule was then suspended in the Bridgman crystal growth furnace and connected to a slow-speed (0.2 rpm) motor. After which, the polycrystalline material was heated slowly (~ 10°C/hr) to 980°C for GaTe in computer controlled three-zone vertical furnace. A computer-operated pre-programmed controller regulates its translational downward motion while the crystal is directionally solidified.

The identical growth procedure was also used for the preliminary growth of the ternary GaSe(1-x)Te(x) crystal with potential nonlinear optical activity. For values of x between 0.1 and 0.3 it is expected that the system should crystallize in the noncentrosymmetric hexagonal structure of GaSe.

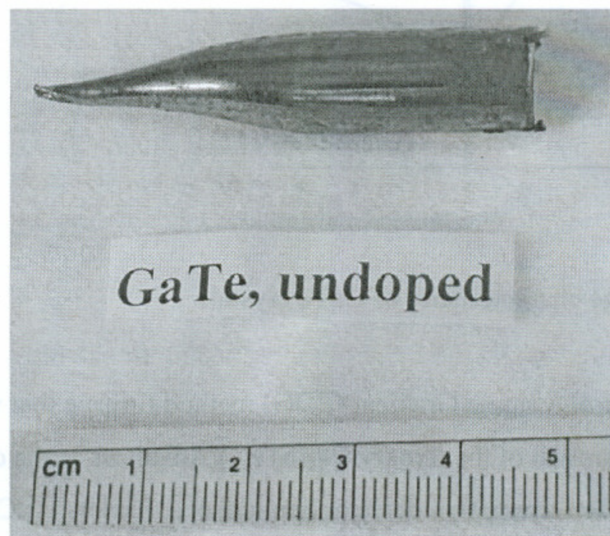

Fig. 6. Photograph of an undoped single crystal of GaTe

The room temperature resistivity of the as-grown and vacuum and Te-annealed GaTe crystals were also measured from current-voltage characteristics as shown in Figure 7

	Resistivity (ohm-cm)
1) GaTe- undoped	$5x\ 10^1$
2) GaTe-Undoped Annealed (7 days)	
a) at 350 C in Vacuum	$8x10^1$
b) Annealed at 350 ^{0}C in Te overpressure	$3x10^4$

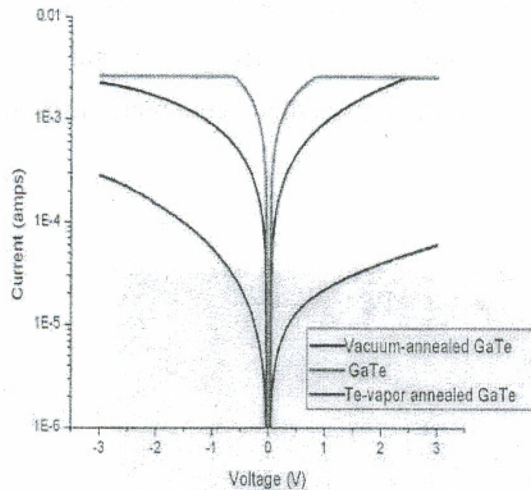

Fig. 7 Current-voltage characteristics of GaTe crystals

GaTe using the ElectroDynamic Gradient (EDG) method furnace that was decribed in the literature for the growth of the ternary CdZnTe. [Advances in the crystal growth of semiinsulating CdZnTe forradiation detector applications, Szeles, C.; Cameron, S.E.; Ndap, J.-O.; Chalmers, W.C. Nuclear Science Symposium Conference Record, 2001 IEEE Volume 4, Issue , 2001 Page(s):2424 – 2428]. The system is PC controlled and allows an operator to enter a desired thermal gradient and its translation rate. The growth occurs without any moving parts. EDG technique nearly completely eliminates the uncontrolled radiative heat transport commonly encountered in traditional Bridgman systems where the charge and furnace move relative to each other. The cooling rate was 1 C/h up to 700 C then 6 C/ h to 20 C. The ingots consist of single crystal with the cleavage plane parallel to growth axis. We have also noticed that the last-to-freeze section was slightly concave. The ingots will be cut (diamond impregnated steel wire)

perpendicular to the growth axis then the sections were further cleaved perpendicular to the growth plane.

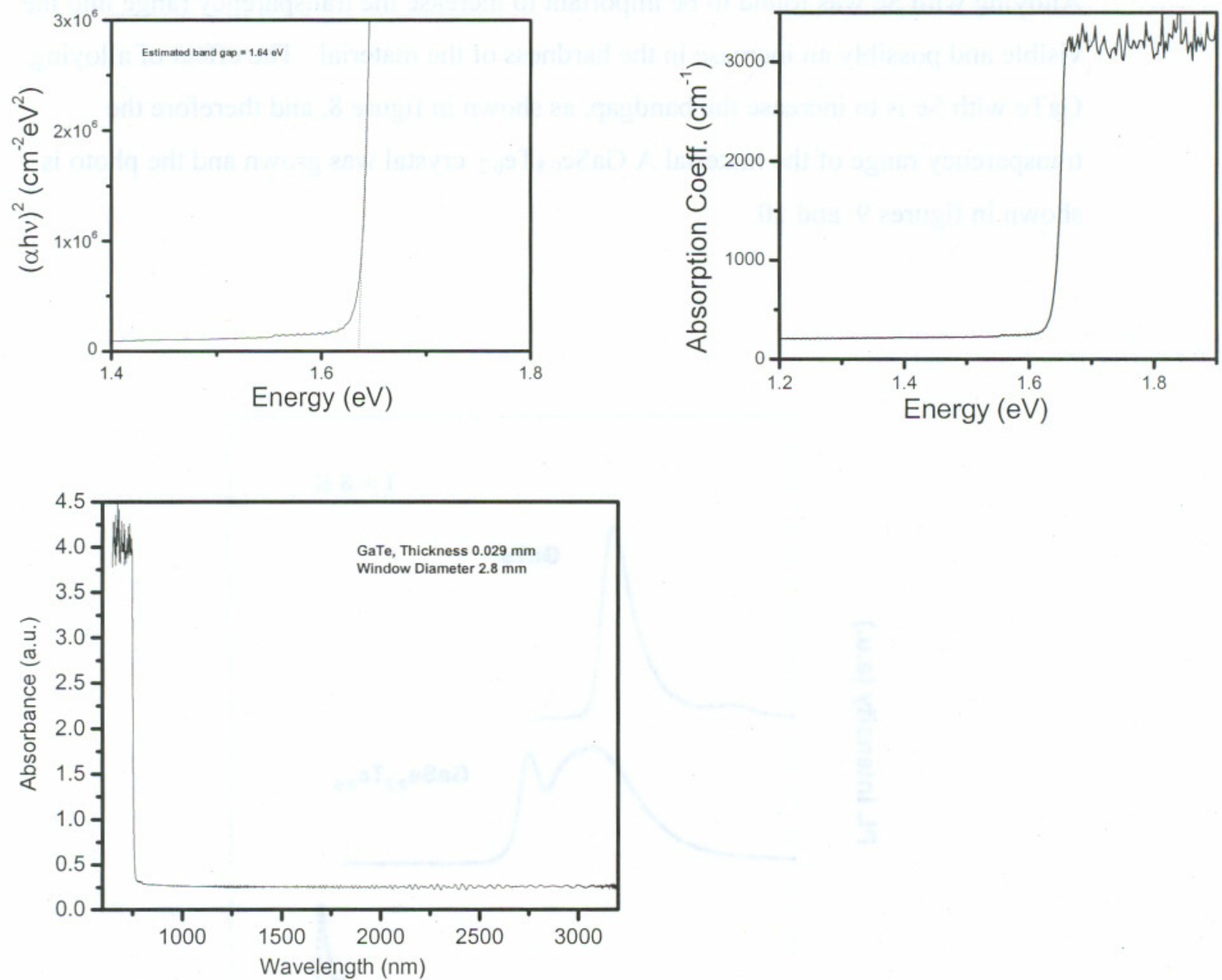

Fig. 7 Absorbance spectrum of GaTe in the near and mid-IR

The thickness was 0.029 mm, measured by SEM. The value of the band gap of GaTe is 1.67 eV and consistent with past literature data. [M. Abdel Rahman and A.E. Belal "Single crystal growth and optical energy gap of gallium telluride," J. Phys. and Chem. of Solids, vol. 61, no. 6, pp. 925-929 (2000)]

Finally, in consultation with Dr. Goldstein at AFRL we have decided that increasing the selenium composition to $GaSe_{0.8}Te_{0.2}$ would be even more beneficial regarding the nonlinear optical properties.

Alloying with Se was found to be important to increase the transparency range into the visible and possibly an increase in the hardness of the material. The effect of alloying GaTe with Se is to increase the bandgap, as shown in figure 8, and therefore the transparency range of the material A $GaSe_{0.8}Te_{0.2}$ crystal was grown and the photo is shown in figures 9 and 10.

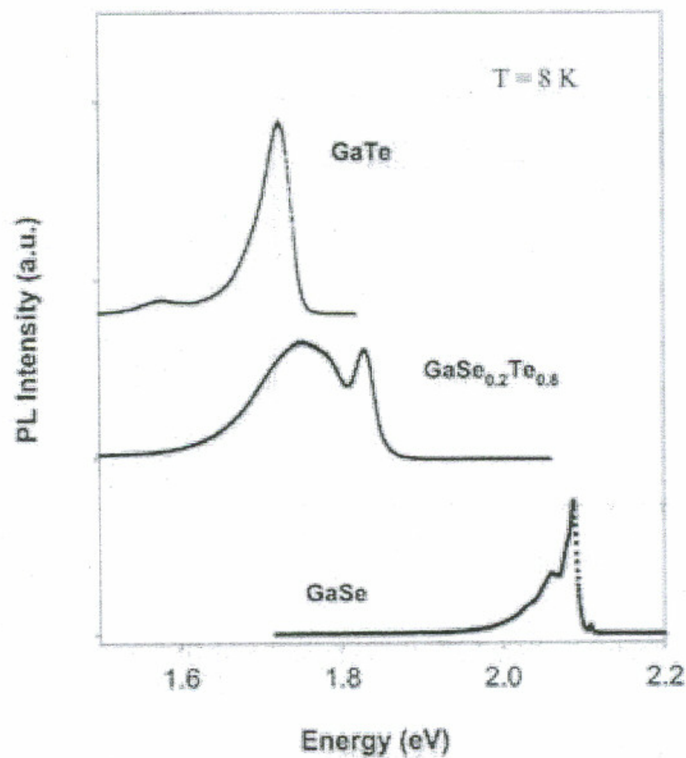

Figure 8. Low temperature photoluminescence of GaTe, GaSe (EIC) and GaSe0.8Te0.2 The effect of alloying GaTe with Se is to increase the bandgap and therefore the transparency range of the material

Figure 9. Photograph of a $GaSe_{0.2}Te_{0.8}$ crystal after being sectioned with a wire saw.

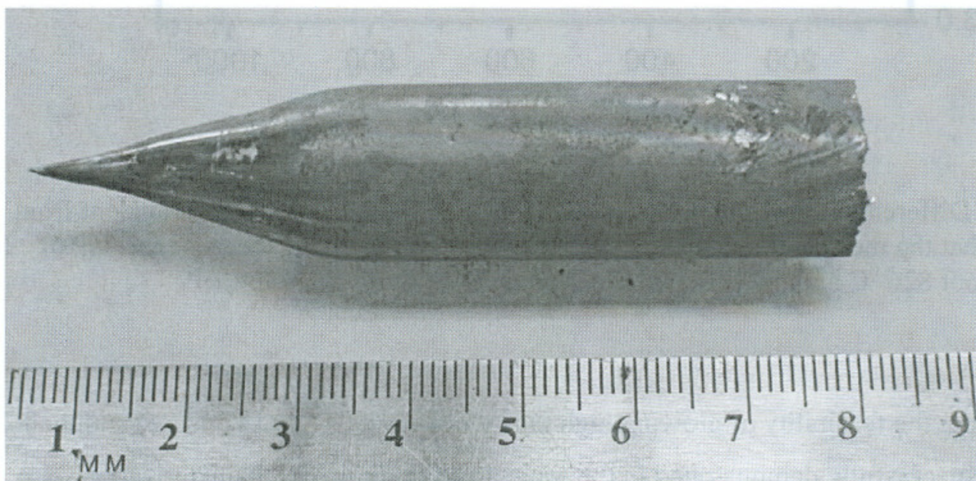

Figure 10. Photograph of an as-grown ingot of GaSe0.8Te0.2

A phase change is also observed just below the MP of the material as shown in Figure 11. This phase change restricts the fast growth of the crystal, and eventually, the crystal is being grown at a very slow rate.

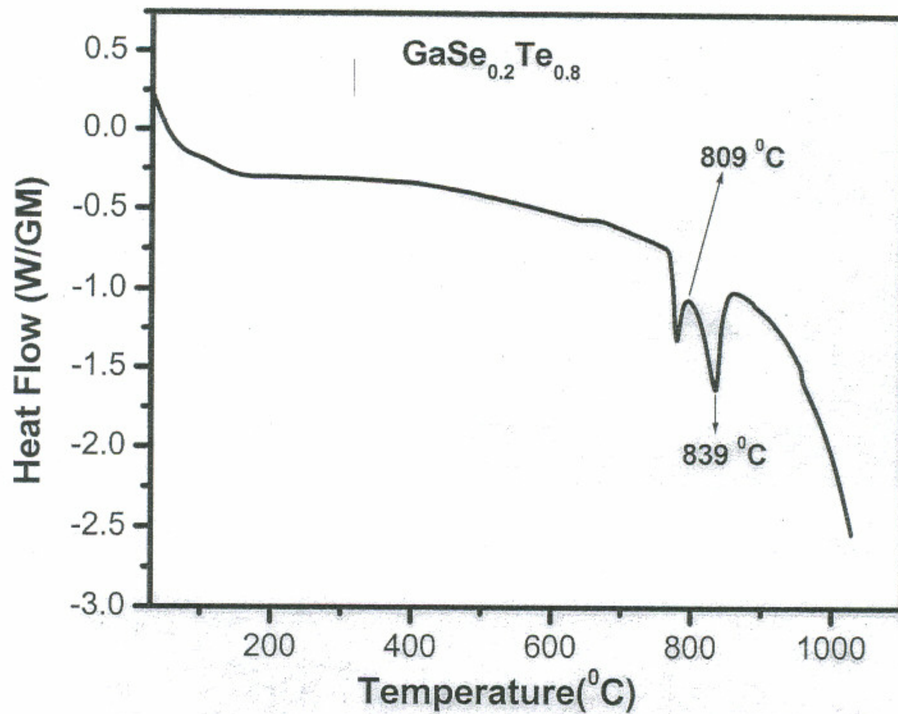

Figure 11. Differential Scanning Calorimetry (DSC) of GaSe0.2Te0.8. It is evident from the figure that the melting point is about 809 ^{0}C, which is surprising, because the MP of GaTe is about 826 ^{0}C and the MP of GaSe is about 960 ^{0}C.

In conclusion, the feasibility of growing high purity GX crystals (X=Te and Se) and their alloys was successfully demonstrated in the project and preliminary characterization indicates that stoichiometric compounds and large single crystalline sections can be obtained.