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Title: "Bulk Growth and Characterization of Quaternary I-III-VI$_2$"

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14. ABSTRACT

Bulk chalcopyrites are essential materials for any second harmonic generation (SHG) or optical parametric oscillation (OPO) applications. These materials are from a class that has been described as the "keystone" for future systems and which will provide a defense for aircraft against heat seeking missiles, a significant threat. Additional these materials may have applications in systems that can detect chemical and biological warfare agents via remote spectroscopy of the atmosphere. The focus of the research was on the development of chalcopyrite materials having improved optical properties, characterization and modeling of the basic physical properties of this class of materials and exploring their implementation in new or improved devices.

15. SUBJECT TERMS

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Introduction

Bulk chalcopyrites are essential materials for any second harmonic generation (SHG) or optical parametric oscillation (OPO) applications. These materials are from a class that has been described as the "keystone" for future systems and which will provide a defense for aircraft against heat seeking missiles, a significant threat. Additionally, these materials may have applications in systems that can detect chemical and biological warfare agents via remote spectroscopy of the atmosphere. It is proposed that alloying two ternary chalcopyrites such as $AgGaSe_2$ and $AgGaTe_2$ can enhance the nonlinearity for the compound quaternary chalcopyrites. Ohmer et.al. proposed that $AgGa(Se_{1-x}Te_x)_2$ with Te = 19 % can exceed the conversion efficiency of $AgGaSe_2$ by more than 100 %. In this period of performance in the project we have designed, purchased, assembled and characterized two new crystal growth systems to be used for the growth of $AgGa(Se_{0.8}Te_{0.2})_2$ [AGST] quaternary chalcopyrites and continued the growth and characterization experiments.

Achievements in the projects

Several investigators have grown chalcopyrites by the horizontal gradient freeze and horizontal Bridgman techniques, respectively. We have investigated the growth of chalcopyrites by the vertical Bridgman technique in a furnace with accelerated crucible rotation technique[1] (ACRT) capabilities.

Efficient mixing can achieved through the use of ACRT 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. We have good reason to believe that is true, since great improvement in the uniformity of the synthesized polycrystalline) charge was also achieved through better mixing (rotation of the ampule held at 45° with respect to normal, procedure developed at Fisk in the previous stage of the project) The growth procedure we have developed at Fisk for the growth of $AgGa(Se_{.8}Te_{.2})_2$ is described below.

The compound was first synthesized from the high purity elements. 5N purity Se, 6N purity Ag, 7N purity Ga and crystal grade Te was used as starting material. Stoichiometric amount of these elements were loaded in a 2mm thick walled quartz tube with inner diameter of 16mm and subsequently sealed under a dynamic vacuum of 6.5×10^{-7} torr. The ampoule was then placed inside a muffle furnace placed ~45° to the horizontal axis. The temperature of the furnace was slowly raised to 780°C. The material was synthesized at 780°C for 48 hrs, during synthesis the ampoule was rotated at a speed of ~ 20 rpm. After synthesis the molten material was quenched in water.
The synthesized material was then placed in a pre baked at 850°C flat horizontal PBN boat. The boat was pre baked at 850°C under a dynamic vacuum of 5×10^{-7} torr. $AgGaSe_2$ was used as a seed, melting point of which is much higher than the quaternary. The loaded boat was then sealed in a quartz ampoule at 5×10^{-7} torr. A three zone semi transparent gold coated horizontal furnace was used for growth purpose. Temperature of the furnace was increased slowly to 787°C, the molten material was kept for 2 days for

stabilization. The furnace started pulling at a speed of 2 cm/day, keeping the ampoule static. After complete solidification of the entire ingot, the temperature of the furnace was started cooling down to room temperature at a rate of 15^0C/day. The total length of the ingot was ~15cm.

The composition measured by EDS near the tip and the tail of the ingot is listed in Table 1.

Table 1. Atomic concentration of the grown crystal near the tip and the tail (last to freeze) part of the ingot at two different positions.

| Sample Postion	Elements	At. %	At. %
Near Tail	Ag	23.8	25,8
	Ga	23.9	23.8
	Se	32.8	33.5
	Te	13.5	12.4
Near Tip	Ag	23.7	23.8
	Ga	31.3	31.4
	Se	39.3	38.6
	Te	5.7	6.2

Additional activities in the project included:

1) A two zone transparent oven has been assembled for crystal growth of AGST. We have presently two such systems fully functional and being used for chalcopyrite growth

2) A boron nitride boat suitable for seeded growth was designed and will be used for future experiments. As a new feature we have designed this time tapered edges (an angle of approx. 10deg) that has been proven to facilitate the extraction of the ingot after the growth

3) An ElectroDynamic Gradient (EDG) growth method was assembled and is being tested. Several problems were identified and we are working with the vendor on several software fixes. After a "training" procedure the system allows an operator to enter a desired thermal gradient and its translation rate. The growth occurs without any moving parts.

4) In one experiment we have tested boron oxide (B_2O_3) as an encapsulant for $AgGaTe_2$, to reduce vapor losses during growth. The melting point of an AGT sample was determined to be 719 °C using thermogravimetric analysis performed with a TA instruments model SDT 2960. After the AGT was melted in contact with molten boron oxide, the melting point of the AGT changed to 707 °C, indicating a possible reaction between the two materials, thus precluding the use of this encapsulant for AGST.

5) The resistivity of the AgGaTe$_2$ samples was found to increase from the first-to-freeze portion to the tail end of the ingot. It varies from 2.3x10^3 Ω •cm to 3.5x10^4 Ω •cm from the beginning to the end of the ingot. The lower resistivity near the starting end of the ingot might arise due to native defects because of the slight off stoichiometry as shown in Fig.2. Thus the higher optical absorption and lower resistivity near the beginning of the ingot are consistent with our EDS data. However, the resistivity of the fast cooled sample was found to be 8 Ω•cm, which is 3-4 orders of magnitude lower than the slow cooled samples. It was previously reported by Bell and Shay (2) that the resistivity of AgGaTe$_2$ samples containing Te rich inclusions increased after thermal annealing in vacuum. In our fast cooled samples we also observed no Te rich precipitates. This possibly explains why the resistivity of the samples cooled at a slower rate was higher than those cooled at a rapid rate. The observed lower band gap (1.09 eV) for the fast cooled sample compared to the other samples might be due to a compositional disorder or deviation from stoichiometry.

6) Figures 1 and 2 show the Raman spectra for the as grown samples of AgGa(Se$_{0.8}$Te$_{0.2}$)$_2$ near the tip of the ingot and near the end of the ingot. Raman spectrum for the tip end of the ingot shows three distinct Raman line at 267.3 cm^{-1}, 243.3 cm^{-1}, and 170.8 cm^{-1}. These are the AgGaSe$_2$ like modes. The corresponding Raman lines for AgGaSe2 reported in the literature are 275 cm^{-1}, 253 cm^{-1}, and 181 cm^{-1}. In this present case for quaternary alloy with Te, the peaks were shifted towards the lower frequency. For the sample near the tail end of the ingot, the peaks were further red shifted to 260 cm^{-1} and 16 cm^{-1}, which is expected because of the sample is more Te rich as compared to the tip end. This behavior is similar in nature for CdS$_{1-x}$Se$_x$ system. Where CdSe like mode shifts towards lower frequency side with increase in sulfur concentration (3).The peak at 243.3 for the tip end has been reduced drastically for the sample near the tail. This might be due to the different orientation of the samples. The line shape of these peaks are broad and clearly asymmetric in nature, on the lower frequency side. This broadening and asymmetry might be due to alloy disorder, similar to CdS$_{1-x}$Se$_x$ system reported earlier (3,4). Disorder activated broadening was also observed in our PL spectra shown in figures 3 and 4.

In conclusion, we have investigated the growth and characterized quaternary chalcopyrite crystals in a system of interest for nonlinear optical applications in the infrared. Large grain polycrystalline AgGa(Se$_{0.8}$Te$_{0.2}$)$_2$ crystals were grown. This crystal was found to be more prone to crack than their ternary alloy analogues. Optical absorption and PL showed large broadening that might be due to lattice disorder. Disorder induced broadening was also observed in Raman spectra.
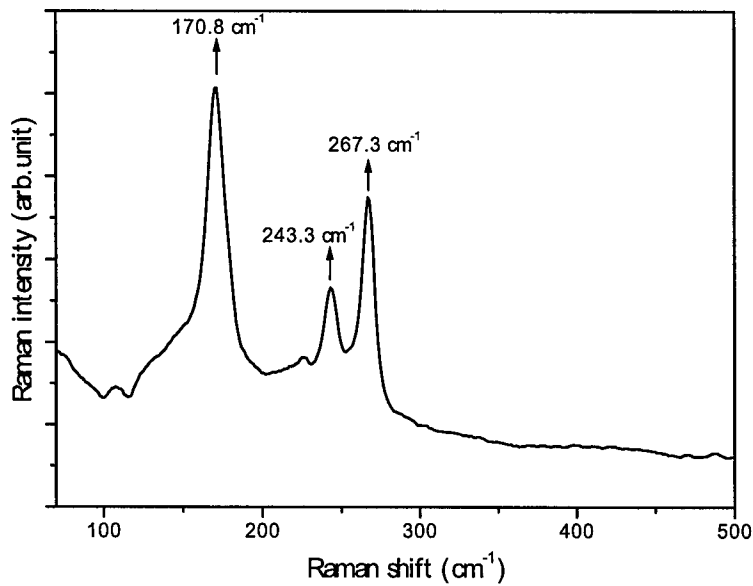
Figure 1. Room temperature Raman spectra for the as grown sample, excitation wavelength is 632.8 nm near tip (first-to-freeze) section of the ingot
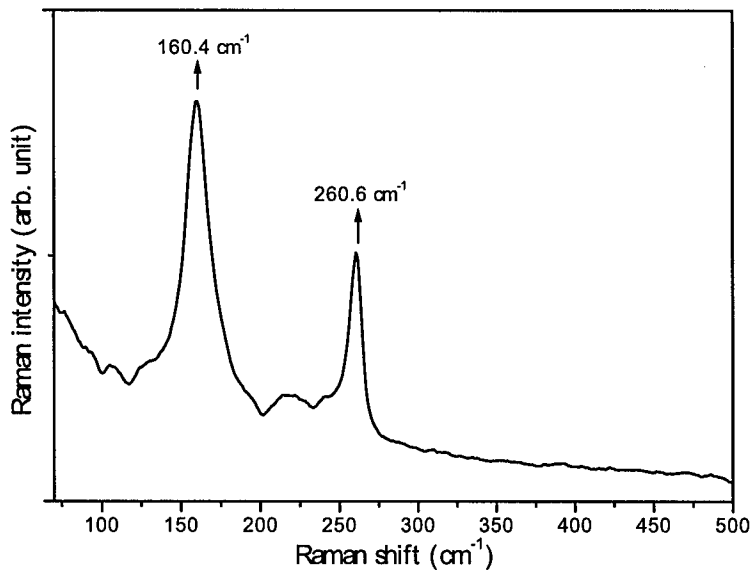
Figure 2. Room temperature Raman spectra for the as grown sample, excitation wavelength is 632.8 nm near the tail (last-to-freeze) section of the ingot
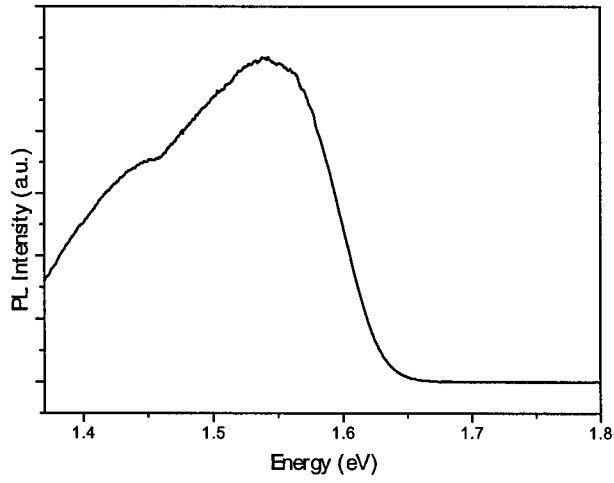
Figure 3. Photoluminescence spectra of the as grown crystal at 10K, excitation wavelength is 0.488μm, near tip
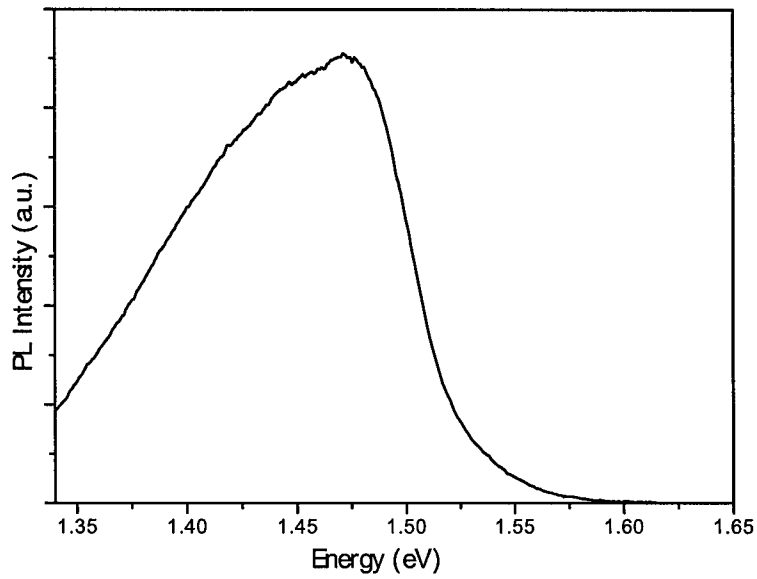
Figure 4. Photo luminescence spectra of the as grown crystal at 10K, excitation wavelength is 0.488μm, near tail.

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