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Edward L. Ginzton Laboratory of Physics
Stanford University
Stanford, California 94305

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GROWTH AND EVALUATION OF $AgGaS_2$ and $AgGaSe_2$ FOR INFRARED NONLINEAR APPLICATIONS

Principal Investigators

Robert L. Byer
Applied Physics Dept.,

and

Robert S. Feigelson
Center for Materials Research

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GROWTH AND EVALUATION OF $AgGaS_2$ and $AgGaSe_2$ FOR INFRARED NONLINEAR APPLICATIONS

I. CRYSTAL GROWTH

A. Objectives

The objective of this program is to improve the crystal growth technology for the two chalcopyrite compounds $AgGaS_2$ and $AgGaSe_2$. These two materials demonstrated their promise as important nonlinear crystals for infrared applications ten years ago. However, at the time, a number of werious growth related problems such as cracking, twinning and the occurrence of optical scattering centers made it difficult to obtain high quality specimens in sizes exceeding 1 cm.

Using seeding and precision-tapered fused quartz growth ampoules, we are developing Bridgman/Stockbarger growth technology to grow crack and twin-free boules in increasingly larger dimensions with an ultimate goal of 4 cm crystals harvested obliquely from c-axis boules. We are studying the post-growth heat treatment procedures to understand the solid state chemical reactions and to avoid crystal damage which frequently occurrs during these annealing procedures.

Initially, experiments will be carried out on $AgGaS_2$ (MP = 996°C). $AgGaS_2$ has the advantage of being transparent in the visible part of the spectrum. Subsequently, experiments will begin on $AgGaSe_2$ (MP = 856°C) which is slightly more difficult to evaluate because it is transparent only in the deep red and near IR.

B. Progress to Date

During the second reporting period, growth experiments continued on $AgGaS_2$ crystals. Additional crystal growth experiments were carried out on 2 cm diameter crystals to further ellucidate the problem of breakdown to polycrystalline and cracked boules. Growth experiments on high quality vs twinned and otherwise damaged seeds supported our earlier conclusion that seed quality was the problem. However, at this time the matter has not been absolutely and unambiguously resolved.

Nonetheless, we have moved ahead to the construction of a larger scale furnace system capable of growing 28 mm diameter boules which weigh approximately 200 g (three times the weight of our earlier boules). Initial growth experiments have been very successful and boule quality appears to be at least as good as earlier boules. Boules have so far been either totally twin-free, or at most contain a few in the conical flare-out region where it is of no consequence. Optical scattering centers are present as in the smaller scale boules. Some compositional or impurity banding is usually observed and this may influence the yield of crystals for subsequent heat treatment to a limited degree. Re-growth experiments, typically used to reduce impurities and eliminate excess components, appear to have slightly beneficial effects, but they are not totally effective at removing banding and double the two week growth interval.

We are currently using a single batch, carefully controlled synthesis procedure to produce the starting material. Starting

compositions of stoichiometric composition and of 0.1% excess Ga_2S_3 are being utilized, with so far no apparent differences in the grown crystals.

Refinements in the heat treatment procedures are being carried out to optimize the thermal program and to determine the minimum amount of Ag_2S required to totally eliminate residual scattering. Occasionally, localized residual inclusions remain after heat treatment procedures have been completed. These defects appear as internally faceted voids when seen under the optical microscope. They tend to occur in regions which contained bands or other macroscopic inclusions after growth and no amount of additional heat treatment eliminates them. Crystal dimensions from the 28 mm diameter boules are considerably larger than earlier specimens and oriented 1 cm^2 crystals exceeding 2 cm in active length are now in preparation.

Initial growth experiments are also underway on $AgGaSe_2$ in the 28 mm diameter boule size. Starting material is slightly easier to prepare than for the case of $AgGaS_2$ because no excess vapor pressure problems occur during the synthesis procedures. Only one boule of $AgGaSe_2$ has been grown so far but seeding was totally successful and when evaluated using an IR image converter, it was seen to be free of physical defects. It displayed 4-fold symmetry typical of a single crystal c-axis boule. Additional growth and evaluation experiments on $AgGaSe_2$ are planned.

C. Crystals Supplied to N.A.S.A. During This Period

$AgGaS_2$ 1 cm^3 , Type I , 58°
1 cm^3 , Type 1 , 58°
1 cm^3 , Type 1 , 90°

Additional crystals have been supplied to Professor Byer's group during this period.

II. EVALUATION FOR INFRARED NONLINEAR APPLICATIONS - SECOND HARMONIC GENERATION OF CO_2 LASER RADIATION

Second harmonic measurements were performed using a 1 cm $AgGaS_2$ crystal grown at Stanford Center for Materials Research and a CO_2 TEA laser. The purpose of the measurement was to obtain experimental verification of the calculated conversion efficiency and calculated phasematching angle, and obtain an evaluation of crystal quality. First the CO_2 TEA laser output was characterized. The angle tuned phasematching curve was obtained using 10.591 μm fundamental radiation. A Laue X-ray diffraction measurement was made to determine crystal orientation and phasematching angle. Crystal absorption was measured both with a scanning spectro-photometer and with the CO_2 laser.

A Tachisto model 215 G CO_2 TEA laser was used for these measurements. Laser wavelength was tuned with a 150 ℓ/mm flat grating used in place of the rear reflector. The output mirror was 35% reflecting with 10M radius of curvature. An iris diaphram was used as an intra-cavity aperture to give transverse

mode control. Two Brewster angle windows on the discharge tube provided a polarized output beam. The grating wavelength calibration was obtained by monitoring laser output with an Optical Engineering CO_2 laser spectrum analyzer. The laser would oscillate on a single CO_2 vibrational/rotational transition. Observation of the laser pulse with a fast time response photon drag detector and oscilloscope showed beating of longitudinal modes. About half the pulse energy appeared to be in a 400 ns long nitrogen tail. The structure due to mode beating changed from shot to shot. Typically about one quarter of the pulse energy would be present in seven pulses of 3 nsec duration separated by the 6 nsec round trip cavity transit time. (Fig.1). It was difficult to obtain Gaussian transverse intensity distribution only by adjusting the intracavity aperture. Diffraction rings usually developed somewhere in the existing laser beam. Externally aperturing the laser beam at the first diffraction minimum, however, did result in a Gaussian-like distribution. It is estimated that peak intensity of the resulting laser output is very roughly 6×10^6 W/cm^2.

Second harmonic conversion efficiency and phasematching tuning curves were obtained by simultaneously monitoring incident fundamental energy and generated second harmonic energy.(Fig.2). A portion of the incident fundamental energy was reflected by a beam splitter into a pyroelectric energy detector. The remainder of the fundamental pulse was incident on the nonlinear crystal. The transmitted fundamental and harmonic beam were then incident on 3 mm thick sapphire windows which had no measurable transmission

at 10.6 μm and transmission of 57% at the second harmonic wavelength 5.3 μm. The portion of second harmonic transmitted through the sapphire filter was measured with a second pyroelectric energy detector. The crystal was rotated in a micrometer driven gimbal mount.

The tuning curve that was obtained (Fig. 3) accurately follows the $\sin^2(\Delta k\ell/2)/(\Delta k\ell/2)^2$ dependence of the ideal case. The fact the five of the secondary maxima are displayed so clearly is an indication of good crystal homogeneity. The fundamental wavelength for this measurement was 10.591 μm. Peak incident intensity was approximately 5×10^6 W/cm^2. This value is uncertain because of the mode beating in the CO_2 laser output. The average measured internal conversion efficiency at the phasematching peak is 0.17%. This is consistent with the calculated values to the extent mode beating structure and proportion of pulse energy in the long decay low intensity tail are known. Laue X-ray diffraction patterns were made to check the orientation of this crystal. When X-ray diffraction and angle tuning results were combined the phasematching angle was found to be 74½° ± ½°. This value is closest to the phasematching angle calculated for the Sellmeier equation obtained by Herbst by fitting to Boyd's dispersion data.

Low crystal absorption combined with good optical quality is an indication of high quality crystal growth. Absorption of this $AgGaS_2$ crystal was measured with an infrared scanning spectrophotometer. Crystal transmission was observed to be constant between 2.5 and 8 micrometers indicating losses due only to

Fresnel reflection and aperturing (Fig. 4). The spectrophotometer recording gives absorption coefficient at 10.591 μm of $\alpha = 0.48\ cm^{-1}$. A measurement of transmission at 10.591 μm using the CO_2 laser and energy ratiometer gives transmission of 45.7%. The calculated Fresnel reflection loss at each surface is 17.1%. This gives an absorption coefficient of $0.43\ cm^{-1}$. The absorption at 10.59 μm in $AgGaS_2$ is an intrinsic property of the material due to a three phonon absorption. The low absorption of this crystal in the 0.5 to 8.0 micrometer spectral range indicate good material quality.

FIGURE CAPTIONS

1. Oscillogram of laser pulse. Time increases right to left. Intensity is displayed on the vertical scale.

2. Schematic drawing of setup used to obtain tuning curve.

3. Phasematching curve for 1 cm long $AgGaS_2$ crystal used for second harmonic generation of 10.591 μm CO_2 laser radiation. Note change of scale.

4. Infrared transmission of $AgGaS_2$ crystal used for second harmonic generation and sapphire window used to block 10.6 μm and transmit 5.3 μm.

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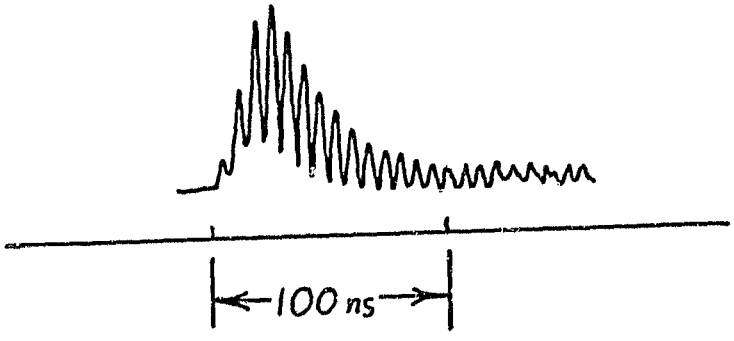

FIGYRE 1

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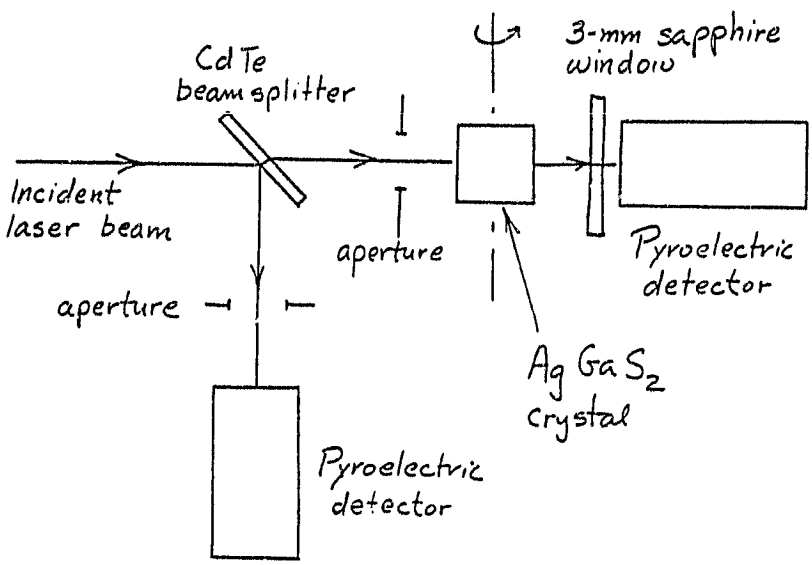

FIGURE 2

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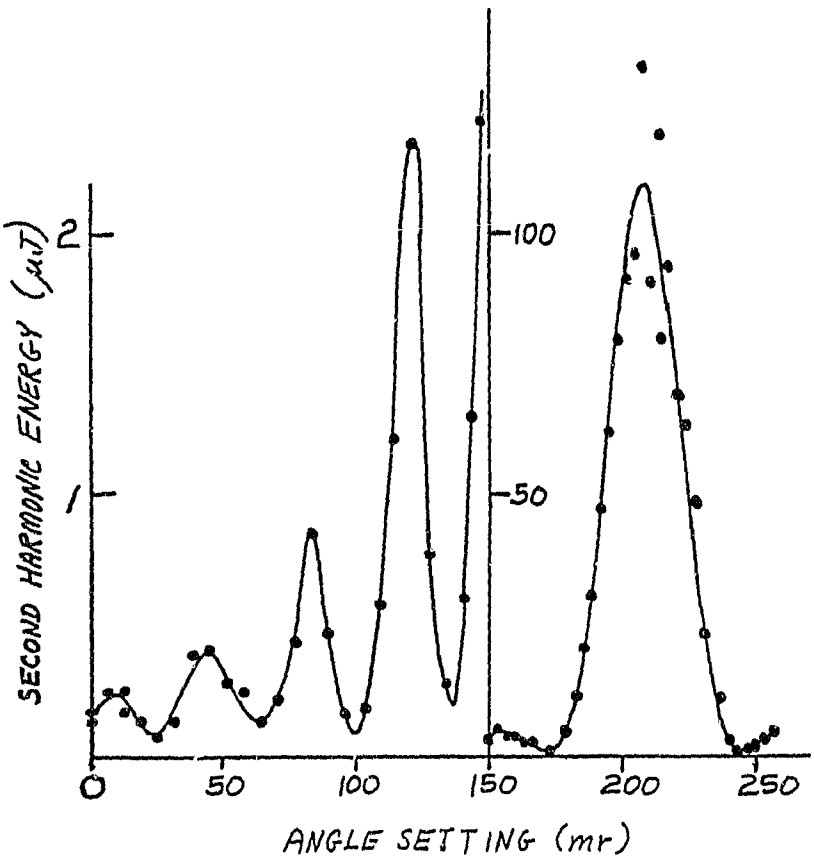

FIGURE 3

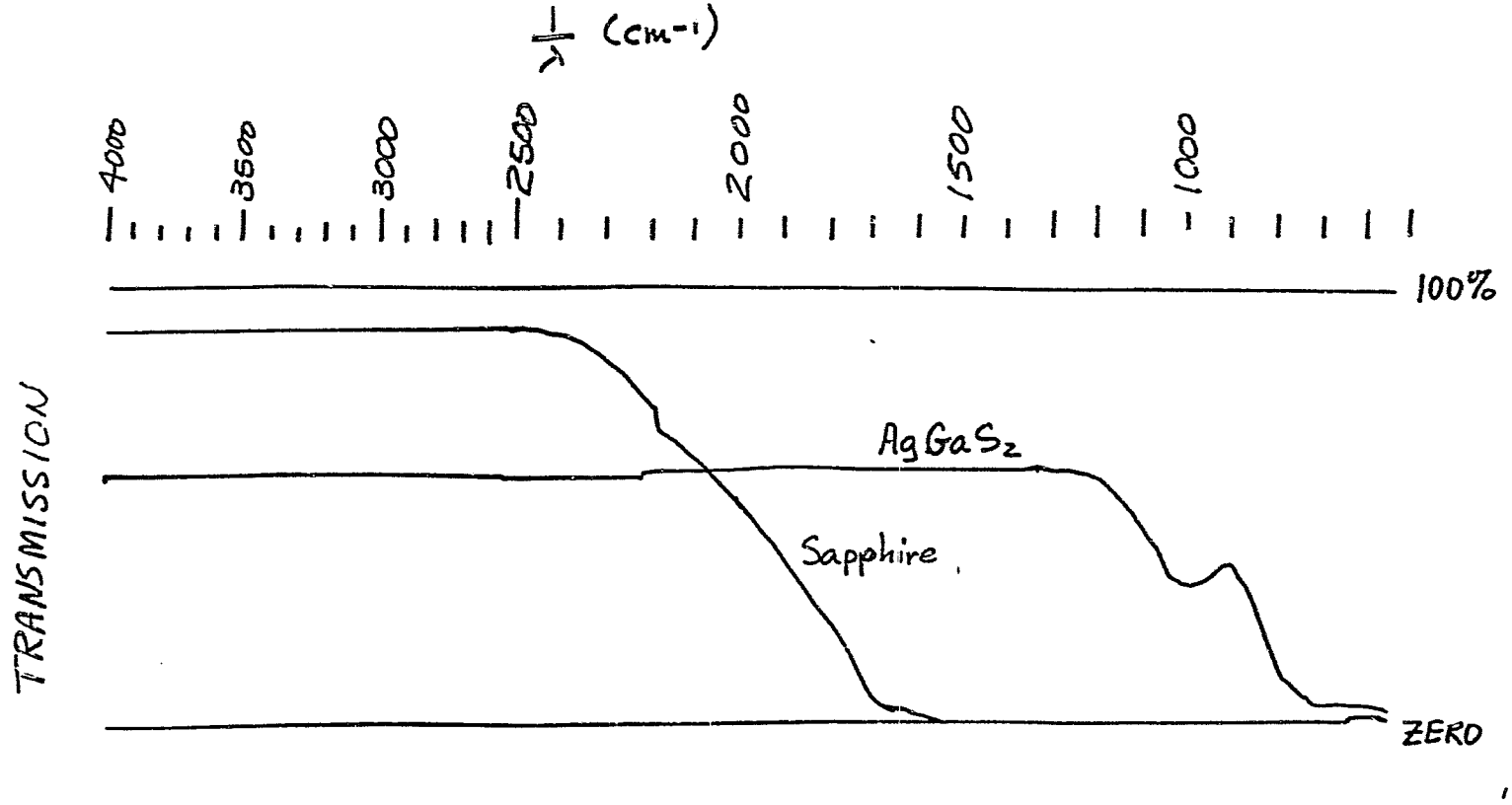

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FIGURE 4