1. ONR Contract Number: N00014-86-K-0343


3. Title of Proposal: Phase Equilibrium and Crystal Growth Studies on AgGaSe$_2$ and Related Nonlinear Optical Materials

4. Name of Institution: Stanford University

5. Principal Investigator: R. S. Feigelson, Professor (Research), Director Crystal Science Division

6. List of Manuscripts submitted or published under ONR sponsorship during this reporting period, including journal references:

None.

7. Scientific personnel supported by this project and degrees awarded during this reporting period.

Scientific Personnel
R. S. Feigelson
R. K. Route
R. J. Raymakers

Students
N. B. Kim
BRIEF OUTLINE OF RESEARCH FINDS
for the period
January 1, 1987 to June 30, 1987

INTRODUCTION

The main objective of this program is to gain an in-depth understanding of the thermodynamics, solid-state kinetics, and growth properties in the Ag-Ga-Se system so that we can reproducibly grow high optical quality crystals of AgGaSe$_2$.

This program began at Stanford on August 20, 1986. During the first four-month reporting period, emphasis was devoted to three areas: growth of 37 mm diameter crystals, increasing our growth capacity so that we can carry out more than one experiment at a time, and studies on the effects of heat treatment parameters on residual scattering centers and residual optical absorption.

PROGRESS TO DATE

During this second reporting period progress has been made in understanding the optical scattering defects which invariably result from the melt growth process. The scattering defects are known to be precipitates which form due to retrograde solubility as the crystals are cooled. Their densities are lowest near the tops of the boules. After a heat treatment procedure which eliminates the vast majority of the scattering defects, remnants remain that cause variable residual optical absorption, and this can have a strong influence on the performance of AgGaSe$_2$ crystals in OPO applications. Careful optical microscopic and SEM studies of heat treated crystals have revealed that at least some of the remnant scattering centers are actually internally faceted voids, or negative crystals, fig. 1. Whether they form during growth or only during the heat treatment procedure is not yet known. Studies are underway on as-grown crystals which are heavily precipitated.

Quenching experiments have also been carried out. We know that the precipitates can be quenched out of as-grown material, proving that there is a single phase existence region of finite width at elevated temperatures. So far,
partially heat treated samples have been quenched from temperatures near 800°C, and remnant scattering centers were found. We have not yet studied quenched samples of as-grown crystals to determine if they too contain scattering remnants. For now we are assuming that the remnants form around large precipitates by vacancy condensation during the heat treatment procedure.

The first experiment to test this hypothesis was inconclusive. The experiment, designed to heat treat the crystal at elevated temperatures before the crystal was ever cooled out of the existence range, was aimed at preventing the precipitates from forming in the first place. We believe there was an error during the initial compounding of the starting material for this experiment, and consequently the charge composition is in doubt. The boule itself was polycrystalline and contained an excessive amount of second phase material. A second experiment to test our hypothesis is now underway.

Due to a lengthy illness of a major contributor to this program, little additional progress has been made in growth related areas. Designs have been completed for additional Bridgman growth capacity, however, and construction is underway on another growth system. We have also taken on an experienced visiting research associate to increase the rate of progress on this program.

SAMPLES FOR EVALUATION

During this period we have fabricated additional SHG crystals of AgGaSe₂ in lengths exceeding 3 cm. These will be made available to staff members at NRL for evaluation. It is anticipated that due to the $x^2$ dependence of SHG conversion efficiency, these crystals should yield higher second harmonic power than previous crystals.
Figure 1 - SEM micrograph of a remnant scattering center in heat treated AgGaSe₂.
END

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