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The results of a joint research program in the development of nonlinear optical devices for the generation of tunable coherent radiation and the growth and processing of the nonlinear optical materials used in these devices is described. Continuous-wave (cw) external-resonant-cavity harmonic generation and optical parametric oscillation have demonstrated the requirement for low losses and good resistance to optical damage in nonlinear optical materials. We have extended cw harmonic conversion to the generation of 1.7 watts of 532-nm radiation using periodically poled lithium niobate and lithium-diffused lithium niobate. We are continuing to investigate the growth technology of the bulk chalcopyrite materials $AgGaSe_2$ and $ZnGeP_2$ and quantum well structures in GaAs for nonlinear infrared applications. A substantial effort has been placed of the characterization of nonlinear materials. Nonlinear optical coefficients have been remeasured in a number of materials to resolve discrepancies that have persisted for two decades, and the optical properties of the lithium diffused lithium niobate have been accurately characterized.

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Growth & Characterization
of Nonlinear Optical Materials

Final Report
for the period
15 July 1988 to 31 October 1991

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Tunable Optical Sources and Synthetic Nonlinear Media / Growth & Characterization of Nonlinear Optical Materials

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Abstract

The results of a joint research program in the development of nonlinear optical devices for the generation of tunable coherent radiation and the growth and processing of the nonlinear optical materials used in these devices is described. Continuous-wave (cw) external-resonant-cavity harmonic generation and optical parametric oscillation have demonstrated the requirement for low losses and good resistance to optical damage in nonlinear optical materials. We have extended cw harmonic conversion to the generation of 1.7 watts of 532-nm radiation using periodically poled lithium niobate and lithium-diffused lithium niobate. We are continuing to investigate the growth technology of the bulk chalcopyrite materials $AgGaSe_2$ and $ZnGeP_2$ and quantum well structures in GaAs for nonlinear infrared applications. A substantial effort has been placed of the characterization of nonlinear materials. Nonlinear optical coefficients have been remeasured in a number of materials to resolve discrepancies that have persisted for two decades, and the optical properties of the lithium diffused lithium niobate have been accurately characterized.

Tunable Optical Sources and Synthetic Nonlinear Media / Growth & Characterization of Nonlinear Optical Materials

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Tunable Optical Sources and Synthetic Nonlinear Media /
Growth and Characterization of Nonlinear Optical Materials

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I. Introduction

The applications for tunable coherent optical radiation have motivated studies of nonlinear optical frequency conversion for more than twenty-five years. These applications range from basic scientific research such as investigations of quantum optics with nonlinear optical devices to entertainment and display such as high-resolution multiple-color projection. The spectral region addressed in this research is the visible to mid infrared, and applications are spectroscopy and remote sensing. There has been recent rapid progress in nonlinear optical frequency conversion due to improvements in nonlinear optical materials and the lasers used to pump the nonlinear frequency conversion processes. Our demonstrations of the generation of visible radiation by external resonant cavity harmonic generation followed by optical parametric oscillation with tunable outputs near the frequency of the pump laser give encouragement that these results can be extended to other spectral regions and other nonlinear materials. The limitations of available nonlinear optical materials become apparent with such demonstrations, and indicate the improvements of nonlinear optical materials required for desired device performance.

This program has been a joint effort that has addressed both the development of nonlinear optical frequency conversion techniques and the growth technology of nonlinear optical materials. The research encompasses a broad area of topics and builds upon the results of previous programs such as ARO contract DAAG29-84-K-0071, which preceded this contract. Only specific topics have been addressed in our research because of the breadth of this field. In the early portion of this contract, we completed work on monolithic $MgO:LiNbO_3$ external-resonant-cavity second-harmonic generators and optical parametric oscillators. Our earlier work with BaB_2O_4 found discrepancy with the published value of the nonlinear optical coefficient of that material. The resolution of this discrepancy lead to the careful remeasurement of the nonlinear optical coefficients of a number of widely used materials with surprizing results. Earlier investigations of the

growth technology of AgGaSe$_2$ have been continued, and we have begun to investigate the growth of ZnGaP$_2$. The work with Li-rich LiNbO$_3$ prepared by vapor transport and solid-state diffusion and periodically poled LiNbO$_3$ grown by a laser-heated pedestal technique was advanced to the point where both materials have been used for continuous-wave (cw) harmonic generation at 1.7-watt second-harmonic output power levels. The investigation of GaAs quantum-well structures has not progressed as rapidly as originally planned. The results that have been achieved in all investigations of this program, however, are significant and of fundamental importance to the field of nonlinear optical frequency conversion.

The demonstrations of second-harmonic generation and optical parametric oscillation in monolithic external resonant cavities has shown the potential of these techniques for efficient cw nonlinear optical frequency conversion. Device operation also clearly showed the performance requirements for the nonlinear optical materials. An essential characteristic for efficient conversion is low loss. A useful figure of merit for a nonlinear optical material is the square of the quantity of the nonlinear coefficient divided by the product the loss coefficient and the index of refraction. The fraction of loss due to absorption is also important because of thermal effects at high average intensity and high average powers that are desired for nonlinear optical frequency conversion applications. The performance lifetime and optical damage at high average intensity of the available MgO:LiNbO$_3$ nonlinear optical material was a limitation of these preliminary demonstrations. Since these demonstrations, MgO:LiNbO$_3$ has been improved, and other nonlinear optical materials have been used with success. The lithium-diffused lithium-rich LiNbO$_3$ and periodically poled LiNbO$_3$ are two new materials developed in this program that overcome some of the previous limitations of lithium niobate.

We have demonstrated external-resonant-cavity second-harmonic generation with both periodically poled and lithium-rich LiNbO$_3$ crystals prepared in this program. The lithium-rich material is prepared by the technique of vapor transport equilibration. Periodically poled material is grown by modulation of laser heating in a miniature pedestal growth process. Both materials have unique characteristics that offer advantages over previous lithium niobate compositions in nonlinear optical frequency conversion applications. We were able to extend harmonic generation from levels of tens of milliwatts to more than a watt with both materials. The growth technology of these materials is in an early stage and remains a topic of investigation motivated by the observed performance.

Our continued investigation of the growth technology of the nonlinear infrared material AgGaSe$_2$ is was directed toward improved growth yield and device performance. As-grown AgGaSe$_2$ crystals contain a high density of precipitates that cause transmission loss

due to optical scattering. Most of the scattering centers can be removed by a two stage postgrowth annealing process in the presence of excess $AgSe_2$. Thermal focusing occurs in the $AgGaSe_2$ material that is now available when powers are increased to approximately 10 watts, a required level for some remote sensing and communications applications. Low thresholds for optical surface damage compared to bulk damage suggest that surface absorption is a likely problem. We have compared surface and volume diffusion in the $AgGaSe_2$-$AgSe_2$ system. We have also discovered some polarization dependent absorption near 2 μm that is apparently related to the scattering centers that form as platelets and rods parallel to the crystal c axis during growth. These investigations are elucidating the processes of thermal annealing and will help to resolve the problems of surface damage and thermal focusing.

Characterization of nonlinear optical materials is essential for device design and engineering calculations of nonlinear optical device performance. We have completed temperature dependent refractive index characterization of different compositions of lithium niobate and absolute measurements of nonlinear optical coefficients of six different commonly used nonlinear optical materials. The refractometry data for the different lithium niobate compositions was not previously available. Values were available for the nonlinear optical coefficients, but the existing data had large discrepancies that needed to be resolved. We have begun calorimetric measurements of absorption in nonlinear optical materials, but the preliminary results are not yet published.

Most of the result of this program have been published in the scientific literature. A list of these publications in given in section IV of this report. Detailed technical information is contained in the publications. Our research results are summarized in section II. Personnel associated with the program are listed in section III.

II. Research Results

A. Tunable Optical Sources

The development of lasers has focussed on the optimization of a few narrow linewidth, single frequency sources. Gas carbon dioxide lasers and solid-state neodymium lasers are now efficient, high-average-power infrared sources at the wavelengths 10.6 and 1.06 μm. Tunable coherent radiation can be generated by the nonlinear optical frequency conversion of these monochromatic sources in appropriate materials. Harmonic generation produces the frequency harmonics of the applied radiation and is now an established technology for Nd:YAG lasers. Optical parametric oscillation and amplification provide a method of generating continuously tunable output.

The relative advantages of nonlinear optical frequency conversion compared to other methods for the generation of near infrared radiation must be considered. For years pulsed OPO's provided the only source of high-power tunable infrared radiation available to chemists. The development of semiconductor diode lasers and doped solid-state ionic crystalline lasers in this spectral range is being intensified. Diode-laser-pumped neodymium doped yttrium aluminum garnet (Nd:YAG) is the best developed laser system with high-power pulsed or cw output and well controlled spectral and temporal characteristics. Diode-laser-pumped thulium and holmium lasers operating near 2 μm are also becoming an efficient high-power source of infrared. Nonlinear optics can extend the the output of these lasers with high efficiency and preserve the temporal and spectral properties of the laser radiation. Thus nonlinear frequency conversion offers some significant advantages for the generation of cw and high-repetition-rate pulsed infrared radiation that have already been realized.

The diode-laser-pump solid-state NonPlanar-Ring Oscillator (NPRO) [1, 2, 3, 4] has proved to be the best source of stable, cw, single-axial-mode radiation for many applications including resonant cavity nonlinear frequency conversion. In an initial demonstration of cw harmonic conversion, Kozlovsky generated 29.6 mW of 532-nm radiation from 56-mW of 1.064-μm pump radiation in a MgO:LiNbO$_3$ monolithic-external-resonant-cavity second harmonic generator.[5] The pump source was the direct output of a Nd:YAG NPRO pumped by a 500-mW diode-laser array. More recently we have generated 6.5 watts of cw 532-nm radiation using lithium triborate (LiB$_3$O$_5$ or LBO) in a discrete-component external-resonant-cavity harmonic generator pumped by 18 W of 1.064-μm radiation.[6, 7] The source of pump radiation was an arc-lamp-pumped cw Nd:YAG laser injection locked by a 40-mW diode-pumped laser.[8] It is expected the semiconductor-diode-laser-pumped Nd:YAG laser will replace the arc-lamp-pumped laser in the near future. We have other research programs that are directed toward the demonstrating a diode-pumped, 10-W, single-longitudinal- and fundamental-transverse-mode laser and a diode-pumped, 100-W diffraction limited slab Nd:YAG laser system.

The OPO experiments that have encouraged us to consider the extension of cw operation into the infrared used the second harmonic radiation described above for pumping. The availability of 532-nm pump radiation and noncritical phase matching with a reasonable temperature tuning range in MgO:LiNbO$_3$ was important for these experiments. Temperature-tuned noncritically phase-matched monolithic resonators provided mechanical stability and low loss for these DRO studies. Pulsed radiation of 400-ns duration and cw 532-nm radiation produced by the monolithic resonant cavity harmonic generator was used to pump the DRO's.[9, 10] The DRO performance was remarkable. The threshold for the

cw device was only 11 mW. Single-mode-pair output was observed routinely from both cw and pulsed DRO's. As much as 80% pump depletion was observed at two times above threshold. The output coupling of the OPO was not optimized for maximum output. Nevertheless, the slope efficiency shown in Fig. 1 was 64% and surprisingly linear. The free-running cw DRO without servo control would oscillate for periods of one minute on a single mode pair. At degeneracy the DRO would stably produce the subharmonic of the pump for periods of 20 minutes. Following these demonstrations, stable DRO operation with servo control has been achieved in other laboratories.[11, 12]
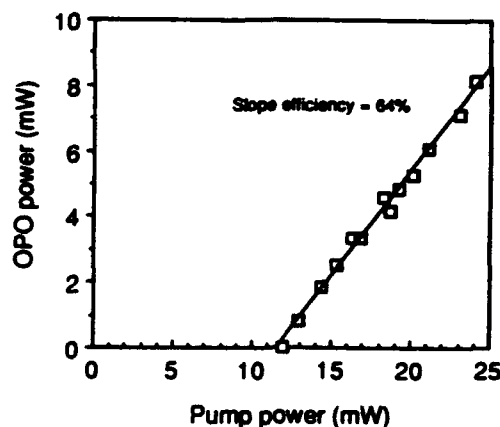

Fig. 1. Output power as a function of pump power for a cw monolithic MgO:LiNbO$_3$ DRO. The DRO was pumped at 532 nm and the output was near degeneracy at 1.064 μm.

The coherence properties of the cw DRO are also remarkable.[13] It was observed during the periods of stable operation between mode hops that the coherence of the outputs of the DRO reproduced the coherence of the pump radiation. When operated on a mode pair adjacent to degeneracy, the signal and the idler difference frequency was stable to better than 1 kHz, the limit of resolution of the measurement. The difference frequency of the signal and the idler is an indication of the additional frequency noise that the DRO adds to that present on the pump radiation. At degeneracy, the output of the DRO was a phase-locked subharmonic of the pump radiation. This was shown by interference of the DRO output and the laser radiation used to generate the second harmonic that was in turn used to pump the DRO.

Our measurements of DRO performance and coherence provided the basis for a theoretical analysis of the frequency-tuning and -control properties of these devices.[14] The analysis showed how three tuning parameters are required for controlling two cavity resonances and phasematching in the DRO. It was possible to model the observed tuning

properties of monolithic $MgO:LiNbO_3$ DRO's using temperature dependent dispersion, thermal expansion, electro-optic, and piezoelectric properties of the material. The analysis is applicable to both monolithic and discrete component cavities. The tuning analysis can be used to calculate the tolerances for stable DRO operation. These tolerances are stringent, for example 0.001°C temperature stability and 5×10^{-10} m cavity length stability are typical requirements. More stringent tolerances than these, however, are achieved in laser frequency stabilization.

Frequency-stable narrow-bandwidth pump radiation is important in the operation of OPO's for a number of reasons. Our measurements with a BaB_2O_4 SRO [15] showed that single-mode pulsed pump radiation improved the output stability by a factor or three compared to multimode pump radiation. The frequency of the pump radiation must be considered a tuning parameter for DRO's, and there is a tolerance of a few MHz required for stable operation.[14] When stable operation of DRO's is achieved, the frequency stability of the pump radiation is present in the DRO outputs. Lasers are now available that provide the required frequency stability for resonant cavity nonlinear frequency conversion techniques. Laser stabilization techniques have advanced to the point that it is an interesting and important challenge to reproduce the available laser frequency stability in the output of a nonlinear frequency conversion device.

More limitations are found in the performance of materials and components. Optical component losses and material losses in the range of 0.1% are now limiting performance. Losses on transmission through nonlinear infrared materials such as $AgGaS_2$ and $AgGaSe_2$ are still in the range of 1% per cm, near infrared materials such as $LiNbO_3$ typically typically have 0.1% per cm loss. Visible materials such as LBO and BBO have perhaps an order of magnitude less loss. These examples are significant improvements over materials losses of a few years earlier, and the availability of these materials has allowed important advances in nonlinear frequency conversion. Material quality, however, continues to be being improved, which is essential for improved device performance. Improvement of the properties of existing materials and development of new materials with superior properties is allowing the extension of nonlinear optical frequency conversion processes to higher efficiency increasing range of application to both higher and lower powers and new spectral regions.

B. Synthetic Nonlinear Media

1. Periodically poled lithium niobate

Periodically poled lithium niobate (PPLN) is of interest for its phase-matching properties and high nonlinear optical coefficient. Recent experiments in which PPLN was used for efficient high-power external-resonant-cavity second-harmonic generation (SHG)

have demonstrated that this material has good potential for nonlinear optical frequency conversion.[16]. Noncritical phase matching is possible in PPLN by choosing the periodicity of the poling to match the coherence length of the desired nonlinear frequency conversion process. Noncritical phasematching eliminates the spatial walkoff between the pump beam and the nonlinearly generated beams. Increased harmonic conversion is achieved when walkoff is avoided. Quasi phase matching (QPM) employing periodic poling also allows different components of the nonlinear optical tensor to be accessed than can be accessed with the more conventional birefringent phase matching. In the case of $LiNbO_3$, the d_{33} component accessible with QPM is seven times larger than the d_{31} component that is accessed with birefringent phase matching. In comparison to visible applications, infrared applications of PPLN require alternating domains with a longer period, which makes the material easier to grow. Absorption and optical damage are expected to be less of a problem at the longer wavelengths. The growth of PPLN is a continuing research topic.

The laser-heated pedestal growth method [17] was used to grow miniature crystal rods with good control of the average growth speed and thus the domain period. To start growth, a carbon dioxide laser is focused on the tip of a source rod to make a small molten droplet into which a seed crystal is dipped. The location of the freezing interface during the growth is determined by the thermal properties of the heated zone and the location of the heating laser focus. The small dimension of the molten zone and the large thermal gradients in this growth result in a freezing surface with a precisely controlled position. The domain periodicity, which depends on the average freezing speed, thus accurately reflects the pulling speed of the crystal rod as it is being grown. Domain reversal is achieved by periodically modulating the heating power, leading to a periodic variation in magnesium dopant concentration. Using this technique, the useful number of domains for first order quasi phase matching in LiNbO3 has been shown to exceed 230.[18]

High-average-power quasi-phase-matched nonlinear frequency conversion was demonstrated using external-resonant-cavity second-harmonic generation.[16] A 1.24-mm-long PPLN sample with 3.47-μm domain lengths was placed in a bow-tie cavity resonant at the 1.064-μm-Nd:YAG-laser wavelength (Fig. 2a). The cavity was frequency-locked to the laser oscillation using the FM sideband technique. The PPLN sample was placed in the center of the cavity where fundamental beam waist radius was 15 μm. The sample had to be heated to 140°C to compensate for a small error in domain length. With this adjustment, 1.7 watts of 532-nm output power was generated with 4.25 watts of incident 1.064-μm pump power (Fig. 2b). This demonstration shows that periodically

poled lithium niobate can be grown with domain lengths suitable for efficient harmonic generation and operated at high levels of cw harmonic conversion at moderate power.
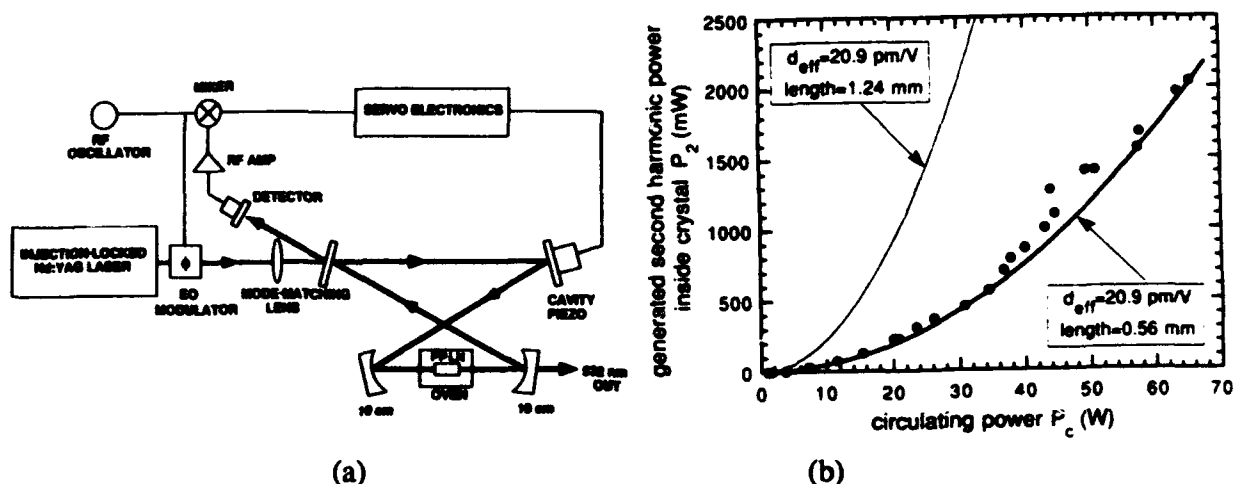

(a)   (b)

Fig. 2. (a) External-resonant-cavity second-harmonic generation of 532-nm radiation in PPLN was observed in a bow tie cavity resonantly locked to the 1.064-μm laser output. (b) Harmonic output power at 532 nm is shown as a function of incident fundamental power. The 1.24-mm-long PPLN sample had 3.47-μm domain spacing.

2. Quantum well structures

Transitions between subbands within the conduction band of III-V quantum wells have interesting mid and far infrared optical properties. These intersubband transitions have large oscillator strengths (typically 15), narrow linewidths (typically 5 meV), and energies in the 50- to 500-meV range controllable with the well width and composition, and are applicable to detectors, modulators, lasers and nonlinear devices in the mid and far infrared. These large matrix elements and resonant enhancements can lead to large nonlinear susceptibilities. However, since square wells are inversion symmetric, their second order susceptibility vanishes, and enhancement occurs only in the third order susceptibilities. Large second order susceptibilities can be obtained in systems in which the inversion symmetry is broken either through asymmetric composition or doping profiles, or through the application of electric field.

We have studied these transitions in electric-field biased AlGaAs wells, and have observed extremely large second-order susceptibilities for second-harmonic generation pumped by 9 - 11 μm radiation, as much as 70 times larger than that of bulk GaAs.[19] These results are in good agreement with a self-consistent field calculation on an effective mass model with corrections for nonparabolicity and band bending. Extending the

calculations to more complex wells such as three layer InGaAs/GaAs/AlGaAs structures or asymmetric doped square wells indicates that nonlinear susceptibilities one or two orders of magnitude larger are possible.

C. Characterization of Nonlinear Optical Materials

1. Nonlinear Optical Coefficient Measurements

More accurate determination of second-order nonlinear optical coefficients is both possible and necessary with the higher optical quality that has become available in laser radiation and nonlinear optical materials. The output of early high power lasers was irregular in temporal and spatial distributions. The irregular nature of these lasers made absolute measurements of nonlinear optical coefficients difficult. Lasers with single-temporal-mode and single-spatial-mode output are becoming common in both high-power-pulsed and continuous wave (cw) operation. It is surprizing that uncertainty and disagreement about the values of nonlinear optical coefficients has persisted. Accurate absolute values are important. Quantitative analysis of nonlinear optical frequency conversion processes is a useful diagnostic tool for determining optimum conditions and avoiding effects that degrade the frequency conversion process. The uncertainty in the nonlinear optical coefficients, however, has made it difficult to perform accurate engineering calculations for nonlinear optical frequency conversion processes.

We have remeasured several nonlinear optical coefficients by the technique of phase-matched harmonic generation.[20, 21] Phase-matched harmonic generation is one of several techniques of measurement and has an advantage of being performed under conditions that are closer to the conditions of practical applications than other techniques. Absolute measurements derived from phase-matched harmonic generation require careful characterization of the pump radiation and detailed attention to phase matching. Both absolute and relative nonlinear coefficient measurements were performed. The following results were obtained: $d_{36}(KDP) = 0.38$ pm/V, $d_{36}(KD*P) = 0.37$ pm/V, $|d_{22}(BaB_2O_4)| = 2.2$ pm/V, $d_{31}(LiIO_3) = -4.1$ pm/V, $d_{31}(5\%MgO:LiNbO_3) = -4.7$ pm/V, $|d_{15}(KTP)| = 1.9$ pm/V and $|d_{24}(KTP)| = 3.5$ pm/V. The absolute accuracy of these measurements is estimated to be better than 10%, and relative accuracy is 4%.

The measurements were initiated because of an inconsistency between the calculated threshold for oscillation in a BaB_2O_4 (BBO) optical parametric oscillator (OPO) and a lower observed threshold.[22] The value of the nonlinear coefficient of BBO [23] that was used for the OPO threshold calculation was relative to KH_2PO_4 (KDP). Some controversy existed concerning the value of the nonlinear coefficient of KDP. The KDP values fall into two groups. The group with lower values have absolute scales derived

from phase-matched second-harmonic generation with either direct measurements of KDP [24] or relative to absolute phase-matched harmonic generation measurements with $NH_4H_2PO_4$ (ADP).[25, 26] A second group with higher values of nonlinear coefficients are based on an absolute scale obtained by parametric florescence measurements on $LiIO_3$. [27, 28] Numerous other interrelations between previous measurements can be found in the tabulations of nonlinear optical coefficients. [29, 30, 31]

Our measure value for KDP is in agreement with the nonlinear coefficient accepted for that material in high-power nonlinear conversion applications,[32] and it agrees with the combination of relative measurements between KDP and ADP and low-power cw absolute second-harmonic measurements with ADP.[30] The ratios of values for KD*P and KDP and for $LiIO_3$ and KDP are in agreement with earlier measurements. The value of d_{31} for $LiIO_3$ reported here, however, is only 58% of the value obtained earlier by the technique of parametric fluorescence. The ratio of $d_{22}(BaB_2O_4)/d_{36}(KDP) = 5.8$ is larger than the value of 4.1 reported earlier. The value of $d_{31}(5\%MgO:LiNbO_3) = 4.7$ pm/V is lower than the value 5.8 pm/V obtained by parametric fluorescence for congruent $LiNbO_3$,[28] but there is a compositional variation in the material involved. The value of $d_{eff}(KTP)$ is more than a factor of two smaller than reported earlier.[33]

Substantiation of these results appears to be developing. We have received a number of private communications in agreement with our measurements. Recent publications describing optical parametric oscillator threshold in KTP [34, 35] and $LiIO_3$ [36] have shown agreement.Recent measurements of the nonlinear coefficient of BBO are also in excellent agreement.[37] Still much remains to be done. The variance between parametric fluorescence and second harmonic generation measurements needs to be resolved. With the current improvements in laser performance and the quality of nonlinear optical materials it is appropriate that nonlinear optical frequency conversion be analyzed quantitatively. Such engineering design and analysis will be useful for characterizing materials, optimizing performance, and increasing the base of knowledge of properties of nonlinear optical materials.

2. Characterization of stoichiometric $LiNbO_3$

Lithium niobate exists over a solid-solution range of 44-50 mole percent Li_2O. Only crystals grown from the congruent melt, however, have good optical quality and birefringence.[38, 39] Unfortunately, crystals of this composition suffer from photorefractive damage when used in nonlinear optical applications involving visible light, e.g. the 532-nm harmonic of Nd:YAG laser radiation.[40] Compositions with higher phase-matching temperature can be operated at temperatures greater than the annealing temperature that removes photorefractive changes.[41] While lithium-rich compositions

have greater birefringence and hence higher phase-matching temperatures, they cannot be grown from the melt without birefringence variations that preclude application of such crystals to optical devices. Lithium niobate crystals of compositions close to stoichiometric with excellent optical quality have been produced by a vapor transport equilibration (VTE) technique.[42]   Phase-matching for 1064- to 532-nm second harmonic generation is observed at 238°C, well above the 110°C annealing temperature.

A temperature dependent dispersion was measured for stoichiometric $LiNbO_3$ obtained by VTE of congruent material.[43]   Dispersion equations of the

$$form \qquad n^2 = A_1 + \frac{A_2 + B_1 F}{\lambda^2 - (A_3 + B_2 F)^2} + B_3 F - A_4 \lambda \qquad were \ fit \ to \ the \ data \ for$$

ordinary and extra indices. Here λ is the free space wavelength in nm, and F is given by $F = (T - 24.5°C)(T - 570.5°C)$ where T is the crystal temperature. The parameters of the equation are are as follows:

	extraordinary	ordinary
A_1	4.546	4.913
A_2	9.17×10^4	1.163×10^5
A_3	2.148×10^2	2.201×10^2
A_4	3.03×10^{-8}	2.73×10^{-8}
B_1	1.93×10^{-2}	9.4×10^{-3}
B_2	5.3×10^{-5}	3.98×10^{-5}
B_3	2.72×10^{-7}	1.6×10^{-8}.

Phase-matching temperatures when in the range of 0°C - 400°C can be predicted to within a few degrees with these equations. These results were confirmed with comparison to measurements made on congruent LiNbO3 and 5%-MgO:LiNbO3 made with the same apparatus.

Congruent lithium niobate is grown deficient in lithium. It can be brought to near the stoichiometric composition by vapor transport equilibration that solid-state diffusion at high temperatures. Lithium-rich lithium niobate fabricated by vapor transport equilibration was used to frequency double the output of a stable single-frequency 1.064-μm Nd:YAG laser. Second-harmonic generation efficiency as high as 69% and powers of as much as 1.6 watts were achieved by external-resonant-cavity second-harmonic generation.[44] The resonant cavity had a bow tie configuration as show earlier in Fig. 2a. The 32-μm-radius pump-beam waist was located in the center of the 1-cm-long crystal. No evidence of photorefractive damage was observed at the operating temperature of 234°C. The effects of

heating due to pump absorption in the crystal, however, were apparent in the roll off of harmonic conversion at higher pump powers.(Fig. 3a) Hysteresis and skewing of the temperature-tuned output power very clearly shows the effects of heating due to pump absorption.(Fig. 3b) The absorption coefficient of the crystal was 0.3% cm^{-1}.
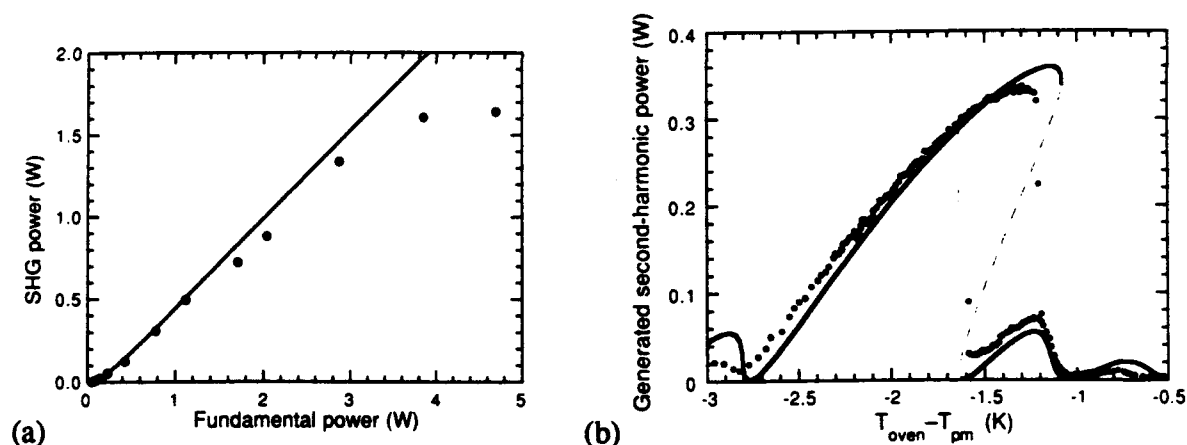

(a)

(b)

Fig. 3. (a) Generated 532-nm harmonic power as a function of 1.064-μm pump power for external-resonant-cavity harmonic generation in a 1-cm-long lithium-rich $LiNbO_3$ crystal. (b) Output power as a function of crystal temperature. The asymmetry is caused by heating due to absorption of pump radiation; 780 mW of power power was incident on the cavity.

3. Absorption measurements in $AgGaSe_2$ and $AgGaS_2$

Silver thiogallate $(AgGaS_2)$[45, 46, 47] is highly transmitting between 0.7 and 9.0 μm, it has a relatively large nonlinear coefficient of $d_{36} = 17$ pm/V, and it has birefringence that will permit type-I angle-tuned phase matching for SHG with fundamental wavelengths between 1.8 and 11.1 μm. The nonlinear infrared materials $AgGaSe_2$ [48] and $ZnGeP_2$ [49, 50] are useful for spectral ranges further in the infrared: 1.6 - 11 μm for $AgGaSe_2$ and 2 - 8 μm for $ZnGeP_2$. $AgGaSe_2$ and $ZnGeP_2$ also have higher nonlinear optical coefficients than $AgGaS_2$. $AgGaS_2$ and $AgGaSe_2$ are available commercially. The growth of $ZnGeP_2$ remains a research topic that is currently being studied at Stanford and other laboratories. We are particularly interested in $AgGaSe_2$ for 2.128-μm pumped OPO's and difference frequency generation in the mid infrared. The growth of both $AgGaS_2$ and $AgGaSe_2$ has been studied at the Stanford Center for Materials Research [51] although more work has been done on the selenide.[52] Both materials have been operated as pulsed SRO's [53, 54] and used for pulsed harmonic generation.[55, 56, 57]

Optical damage considerations, absorption, and thermal properties must be considered anew when make the transition from low-repetition-rate-pulsed to higher-average-power

operation. Earlier measurements of pulsed operation give some insight to optical damage limitations. Working with 20-ns-duration pulses of 10-Hz repetition rate damage threshold in the range of 13 - 30 MW/cm^2 were observed for both $AgGaS_2$ [53] and $AgGaSe_2$.[54] Elsaesser et. al.[58] observed surface damage thresholds of 25 GW/cm^2 for $AgGaS_2$ when irradiated with 100 pulses of 20-ps duration. They also observe the bulk damage threshold about one order of magnitude higher than surface damage. In an $AgGaSe_2$ harmonic generation experiment pumped with 20-ns-duration, 100-kHz-repetition-rate 10.6-μm pulses, we were able to transmit 200 kW/cm^2 average intensity through bulk $AgGaSe_2$; surface damage, however, was encountered at 20-kW/cm^2 average intensity.[57] The order of magnitude difference between surface and bulk damage prevails through widely varying conditions. We were able to focus 17.5 W of cw 1.064-μm radiation to a beam waist w_0 = 35 μm for a peak intensity of 900 kW/cm^2 at the surface of a $AgGaS_2$ crystal and transmit through the surface without damage. This cw threshold is adequate for the pumping intensities required for cw optical parametric oscillation.

Spectrophotometer and laser-calorimeter measurements were performed on several nonlinear optical crystal samples. It was found that many $AgGaS_2$ and $AgGaSe_2$ crystals had absorptions near 2 μm (Fig. 4,5). Laser calorimetry measurements show a strong polarization dependence of these absorptions. For example one $AgGaS_2$ crystal with clear surfaces had absorption coefficient of 1% cm^{-1} for ordinary polarization and 6% cm^{-1} for extraordinary polarization. Fortunately the signal and idler waves near 2 μm in a 1-μm-pumped $AgGaS_2$ OPO with type-I phase matching will be ordinary waves. Calorimeter measurements for three representative crystals of $AgGaS_2$, $AgGaSe_2$ and $LiNbO_3$ are given in Table I. Analysis of the measurements required knowledge of the specific heat, which was also measured for the three materials. A published value for the specific heat of $LiNbO_3$ is listed for comparison. The low values for absorption at 1.32 μm are encouraging. Sample to sample variation of the 2-μm absorption suggests that it may be due to an impurity. These are preliminary measurements, and comparison with spectrophotometer measurements and detailed balance measurements where loss is determined by measuring incident, transmitted and reflected power suggests the calorimetry measurements are possibly low by a factor of two. The calorimetry measurements, however, are not sensitive to scattering.

The sensitivity of phase matching to temperature is relatively small in $AgGaSe_2$ and $AgGaS_2$; for a change of crystal temperature from 23 to 65°C, the phase-matching peak shifts only 0.7 degrees of angle for 10.6- to 5.3-μm harmonic generation in $AgGaS_2$. This is approximately the tuning width for a 3-cm long crystal. This is, however, a relatively strong thermal focusing that is driven by absorption in the crystal. Marquardt at the Naval
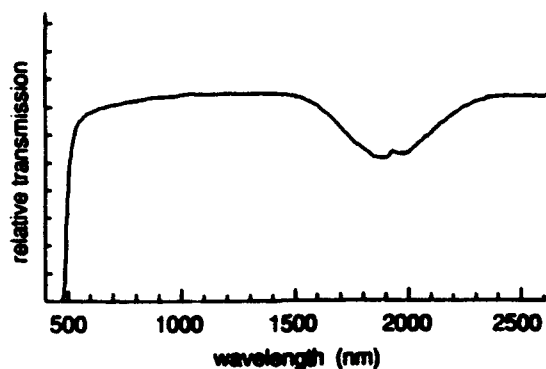
Fig. 4. Transmission of the extraordinary wave in a 90°, 2.3-cm-long $AgGaS_2$ crystal.
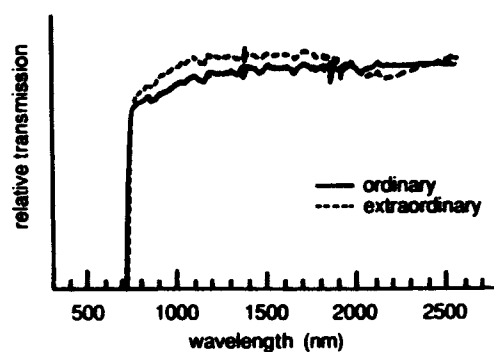

Fig. 5. Transmission of ordinary and extraordinary waves in a 3-cm-long $AgGaSe_2$ crystal. Propagation is at 55° to the optic axis.

Research Laboratory [private communication] has determined the empirical relationship for the focal length of the thermally induced lens

$$F.L. = 270 \text{ cm (W/cm}^2) \, d^2 / \Delta P$$

where d is the diameter of a Gaussian beam at $1/e^2$ maximum intensity and ΔP is the power absorbed in the crystal. Many questions remain to be resolved. Our work with high-average intensity CO_2 beams suggests that the cause of the thermal lensing could be absorption at the surface. With increasing demand for high-average-power operation, it is important the the source of the absorption be determined and reduced.

Table I. Laser Calorimetry Measurements and Related Values for Representative Samples of Three Nonlinear Optical Materials

Material	$AgGaS_2$	$AgGaSe_2$	$LiNbO_3$
sample size	$1 \times 1 \times 2$ cm^3	$1 \times 1 \times 3$ cm^3	$1 \times 1.5 \times 5$ cm^3
measured specific heat $C_w = 4.18$ J/(K°gr)	0.078 C_w	0.061 C_w	0.147 C_w
Published specific heat [59]			0.15 C_w
Density [60]	4.25 gr/cm^3	5.71 gr/cm^3	4.25 gr/cm^3
Absorption coefficients at 1.32 μm			
ordinary wave	0.18%/cm	0.13%/cm	0.13%/cm
extraordinary wave	0.27%/cm	0.16%/cm	0.085%/cm
Absorption coefficients at 2.05 μm			
ordinary wave	1%/cm	0.24%/cm	
extraordinary wave	6%/cm	1.7%/cm	

D. Growth of nonlinear Optical Material

Research in the growth technology and characterization of existing and new nonlinear optical materials has been carried out by the Crystal Science group headed by Professor Robert S. Feigelson. Progress in the growth of the chalcopyrites, silver gallium sulfide and silver gallium selenide ($AgGaS_2$ and $AgGaSe_2$), has resulted in high quality angle phasematched crystals of lengths up to 35 mm. The recent development of beta-barium borate (BBO) has spurred an intensive effort to grow this new material here, and a 12-mm-long crystal has been produced. We have demonstrated that both magnesium oxide doping and lithium in-diffusion of lithium niobate ($LiNbO_3$) substantially reduces the photorefractive damage that has limited the use of this material. Each of these materials has unique features which extends the range of performance of available nonlinear materials. As these and new materials are developed they are evaluated experimentally with various nonlinear conversion techniques.

Silver gallium selenide ($AgGaSe_2$)

Two major objectives were undertaken concerning $AgGaSe_2$. The first involved scaling up the boule size to 40-mm diameter, so that longer, more efficient crystals could be prepared. The second objective was to develop a better understanding of the types of optical defects which form in this material, and the mechanisms by which they form, so that crystals with lower residual absorption can be produced.

1. Growth of large AgGaSe2 crystals

The scaling of boule size was successfully accomplished midway through the program, and a thorough description of the crystal growth procedure is given in publication number 12 of the list in section IV or reference [61]. Boules 37 mm in diameter were successfully produced with good yield, and the technology was transferred to both Cleveland Crystals, Inc. and INRAD, Inc. during the course of the program.

2. AgGaSe2 crystals with improved cutting yield

Because $AgGaSe_2$ crystals for specific nonlinear optical applications must be cut at various angles to the optic axis, the yield of finished crystals from a circular cross-section boule is an important consideration. The development of improved crystal growth technology was, therefore, extended in a study addressing the question of whether $AgGaSe_2$ crystals with controlled crystallographic orientation could be grown in square cross-section ampoules.

$AgGaSe_2$ crystals are typically grown in sealed, fused quartz growth ampoules. Since $AgGaSe_2$ expands along the c-axis during cooling, boules must be seeded so they can expand freely in the growth ampoule, i.e. the c-axis must be aligned closely with the

ampoule axis. Furthermore, it was necessary to control the transverse orientation of the seed, as well, so that a square cross-section seed was required in addition to a square cross-section seed pocket. It was calculated that 31 mm x 31 mm square cross-section boules would have the same yield as 37 mm dia round cross-section boules. To produce square cross-section growth ampoules with the desired interior dimensions and provide for a smooth transition from a square seed pocket to a square body, a vacuum-forming method by which slightly oversized fused-quartz tubing could be collapsed upon a precision-machined graphite mandrel was developed.

Accurately oriented c-axis seeds were hand-fitted to the growth ampoules by a taper grinding method. A few mils clearance was allowed for transverse thermal expansion during heat-up. To achieve an optimum orientation of the square cross-section boules for type I phasematching, the side faces of the seeds were oriented normal to the (110) plane which is the plane in which light propagates during type I phase-matched nonlinear interactions. Crystal growth was carried out at 8-15 mm/day in the manner described in publication number 12. Typically, boules appeared to be of excellent structural quality: no significant differences were apparent when comparing the circular and square crystals, and no evidence of cracking due to stress concentrations in the corners of the square cross-section samples was observed.

Assuming 1 mm kerf losses, approximately 63-64% of a circular cross-section boule was harvestable in slab form compared to 95% from a square cross-section boule. Reuse of the growth ampoules was possible as long as chemical reactions between the melt and the ampoule walls were strictly prevented by the use of a dense, well-adhering pyrolytic carbon coating which is standard practice in the growth of this material.

In addition to the obvious improvement in cutting yield, this work demonstrates that even with materials such as $AgGaSe_2$ and $AgGaS_2$ which display anomalous thermal expansion during cooling, it is possible to grow defect-free single crystals in fused quartz containers having nonconical shapes. The vacuum-forming technology used to produce precisely tapered fused quartz growth ampoules is readily adaptable to small glass lathes with moderate size multiple burner cross-fire torches, and the use of precisely tapered vacuum-formed fused quartz growth ampoules can obviously be extended to more complex geometries depending on specific application requirements.

This particular research project is described in detail in publication number 10 listed in section IV or reference [62].

3. Improvements in the optical quality of $AgGaSe_2$ crystals

The optical defects found in as-grown $AgGaSe_2$ crystals, and which are discussed in detail in the publications resulting from an earlier ARO-supported research program [51], are known to be Ga_2Se_3-rich precipitates. The density and distribution of these precipitates vary with growth conditions. Fortunately these can be removed by heat treatment processing in the presence of $AgSe_2$ with reasonably good results. However, residual scattering defects, which can be observed only after the heat treatment cycle is completed, appear to be internally faceted voids, or negative crystals and usually remain in varying concentrations. Optical scattering from these residual defects, typically in the few % cm^{-1} range and varying somewhat from one crystal to another, has limited the use of $AgGaSe_2$ crystals in resonant applications, although the relative effectiveness of the single cycle heat-treatment procedure has permitted their use in non-resonant applications. While this program was in place, a major breakthrough was made in the development of a video technique for imaging near-IR light scattering in heat-treated $AgGaSe_2$ crystals that allowed us to accurately assess the density of optical defects remaining after the conventional single step heat-treatment process.

A major objective was immediately established to take a more detailed look at the scattering phenomenon in $AgGaSe_2$ using this improved optical characterization technique, to correlate the results with the heat-treatment procedure used, to devise a more effective heat-treatment procedure, and to elucidate subtle details of the Ag_2Se-Ga_2Se_3 phase equilibria which determine the complex growth behavior of this material.

Oriented slabs and crystals of as-grown $AgGaSe_2$ containing precipitates in varying concentrations were heat-treated in the presence of Ag_2Se in evacuated and sealed fused quartz ampoules according to the procedures described previously.[51] The amount of optical scattering due to the presence of precipitates was then evaluated by several methods: 1) low power evaluation using a commercial IR image converter in a transmitted light mode; 2) high power IR microscopic examination in transmitted light; 3) visible high magnification optical microscopic evaluation of thin sections which are reasonably transparent; 4) spectrophotometric transmission measurements throughout the transparency range; and 5) the newly-developed video imaging technique for imaging near-IR scattering under either dark field or bright field illumination. This technique relies on the near-IR sensitivity of video cameras with either silicon vidicon or CCD array detectors, and the high resolution processing of readily available video equipment.

In singly heat-treated $AgGaSe_2$ crystals under dark field illumination, this technique clearly revealed for the first time, the presence of light scattering centers concentrated in a

core region of the crystal. Clear defect-free regions were found near the surface, indicating an incomplete diffusion process. Virtually all the AgGaSe$_2$ crystals studied displayed this effect when heat-treated using the single cycle process. Incomplete diffusion processing was thus for the first time recognized as being responsible for the variability in optical quality from one heat-treated crystal to the next.

Single cycle heat-treatment processing for longer times and/or at higher temperatures was not found to be effective at removing the residual defects. Repeating the heat-treatment procedure using lesser amounts of Ag$_2$Se (on the order of 0.2 wt %) with no direct mechanical contact to the AgGaSe$_2$ crystal under treatment, was found to be effective. A fairly simple determination of the relative improvement in optical quality due to secondary heat-treatment indicated that optical scatter losses were reduced by at least a factor of four. Follow up measurements have indicated that the combined absorption/scatter loss of these doubly heat-treated crystals is less than 1% cm^{-1} in the important 2 μm OPO pump wavelength region, and this is sufficiently low for resonant applications.

This particular research project is described in detail in publication number 11 of the list of section IV or reference [52].

4. Analysis of the heat-treatment processing of AgGaSe$_2$

To better understand the heat-treatment procedure that is essential for eliminating the precipitate phase from AgGaSe$_2$ crystals, a study was undertaken to analyze the process using microchemical analytical techniques, low temperature processing, and reactive diffusion couples which were analyzed by x-ray diffraction, optical microscopy and electron probe microanalysis.

The most common high temperature heat-treatment process for eliminating second phase precipitates utilizes a binary diffusion couple which places AgGaSe$_2$ crystals in direct contact with a small amount (approximately 1.0 mol%) of Ag$_2$Se for three weeks at 800° C in an evacuated and sealed quartz ampoule.[51] Since the AgGaSe$_2$ is usually placed on top of the Ag$_2$Se to ensure good physical contact, the annihilation of second-phase precipitates is expected to proceed from the bottom of the crystal to the top, and thus the transparency of the AgGaSe$_2$ crystal to be greater at the bottom than at the top until the diffusion process has gone to completion. However, dark field IR scattering measurements using the silicon vidicon imaging technique described in the previous section showed that annihilation proceeds uniformly inward from all free surfaces of the crystal, regardless of the distance to the Ag$_2$Se annealing medium. Previous studies in our laboratory had demonstrated that vapor phase transport plays only a minor role in the heat

treatment process, and therefore, a clear understanding of the heat treatment process was lacking.

In this study, chemical reactions occurring during heat-treatment were analyzed at several temperatures below the eutectic temperature using reactive diffusion couples between as-grown $AgGaSe_2$ crystals and polycrystalline Ag_2Se, and standard (chemical inter-) diffusion couples between as-grown $AgGaSe_2$ crystals and polycrystalline Ag_9GaSe_6, an intermetallic compound in the Ag_2Se-Ga_2Se_3 pseudobinary system that is in phase equilibrium with stoichiometric $AgGaSe_2$. In the reactive diffusion couples that are representative of the commercial heat-treatment process, but which were processed in this study at a lower temperature to avoid complications caused by the formation of a liquid phase at the interface, we observed formation of the intermediate A_9GaSe_6 phase both normal to the mechanical interface, and along the free surface. Analyzing the microchemical analytical data to determine the relative surface and volume diffusivities for silver, D_S^{Ag} and D_V^{Ag} respectively, we found

$$D_S^{Ag} = 5.43 \times 10^{-4} \exp(-0.46 \, eV/kT)$$

and

$$D_V^{Ag} = 2.40 \times 10^{-7} \exp(-0.84 \, eV/kT).$$

It can readily be seen that at all temperatures, surface diffusivities were much larger than volume diffusivities.

Initially, it was assumed that Ag would turn out to be the principal mobile species. It was found, however, that the volume diffusivities for Ga and Se in the $AgGaSe_2$ phase were approximately the same as that for Ag. We also found that the volume diffusivity of Ag at 700° C (approximately 1×10^{-11} cm^2/s) was much lower than typical values for Ag diffusivity at 700° C in GaAs (approximately 3×10^{-8} cm^2/s) and for Ag diffusivity at 700° C in $Hg_{0.8}Cd_{0.2}Te$ (approximately 1×10^{-9} cm^2/s). Self-diffusion studies of Se in CdSe and chemical interdiffusion studies of Se in CdTe, on the other hand, revealed diffusivities on the order of 10^{-11} cm^2/s at 700° C, much closer to the values determined in this study. Since our experimental diffusivities are more characteristic of Se (anion) rather than Ag (cation) diffusion, we postulate that the diffusivities measured here are those resulting from a cooperative phenomena among Ag, Ga and Se atoms, where Se may move together with Ag and Ga to maintain binary (Ag_2Se and Ga_2Se_3) stoichiometry and electroneutrality, and that the diffusion kinetics of Se are the rate limiting mechanism.

From the experimental results of this study, the uniform annihilation of second-phase precipitates in $AgGaSe_2$ samples during high temperature heat-treatment can be postulated

to occur as follows. The intermetallic compound, Ag_9GaSe_6 forms initially at the Ag_2Se-$AgGaSe_2$ interface as a result of reactive diffusion, rapidly covers the entire surface of the $AgGaSe_2$ sample before significant volume diffusion occurs because of the high rate of surface diffusion. (The formation of a liquid phase during high temperature heat-treatment processing may even facilitate the surface migration process beyond that observed here.) Volume diffusion of the Se anion with its slower kinetics then becomes the rate limiting mechanism in the heat treatment process, and this accounts for the fact that diffusion appears to proceed uniformly inward from all surfaces of the crystal.

It is still not known what defect allows for the excess solubility of Ga_2Se_3 in $AgGaSe_2$ at elevated temperatures, nor is it known for certain whether this Ga_2Se_3 excess is eliminated through out-diffusion of Ga_2Se_3 or by in-diffusion of Ag_2Se. Mass balance studies on the closely-related nonlinear material, $AgGaS_2$ have demonstrated that Ga_2S_3 does in fact out-diffuse from the matrix during heat-treatment processing. Preliminary studies in our laboratory have indicated that the selenide system may behave similarly, but this has not yet been unambiguously demonstrated and further investigation in this area is warranted.

This particular research project is described in detail in publication number 14 of the list of section IV or reference [63].

E. Summary and Future Directions

In this program, we have investigated limited number of specific topics in a broad area. The requirements of nonlinear frequency conversion do cover a larger range of materials characteristics and device specifications. Our topics of investigation were chosen to make our effort most productive. We have investigated new materials including GaAs quantum wells, $ZnGeP_2$, periodically poled $LiNbO_3$, and stoichiometric $LiNbO_3$. We have achieved improved performance over earlier lithium niobate compositions with the periodically poled and stoichiometric materials; this was demonstrated by the generation of more than 1 watt of 532-nm cw radiation produced by external-resonant-cavity second-harmonic generation pumped at 1.064 μm. We have performed the temperature dependent refractive index characterization of stoichiometric $LiNbO_3$ necessary for application specifications. Our remeasurement of nonlinear optical coefficients of six commonly used nonlinear optical materials appears to be gaining acceptance as a new standard. Our continued investigation of the growth and characterization of $AgGaSe_2$ is increasing our understand of this material leading to improvements in optical quality required for cw and higher power applications.

Future work needs to concentrate on improved material for for cw and higher average power applications. A goal of our research is to generate cw and pulsed sources of widely

tunable infrared radiation at high conversion efficiency and with good reliability. The chalcopyrite materials $AgGaSe_2$, $AgGaS_2$, and $ZnGeP_2$ have shown significant improvement, but further improvement is required. This seems to be universally true of all nonlinear optical materials. After an improvement in material characteristics, the applications immediately advance until the new limits of the material reached. Lithium niobate is an example. Our early investigations were limited by damage at the 100-mW level in $5\%MgO:LiNbO_3$, but now we are limited by thermal distortion in stoichiometric $LiNbO_3$ at pump powers of several watts. Improved optical quality with reduced losses is a common requirement of nonlinear optical materials for many applications. The properties are need for both stable and efficient cw nonlinear optical frequency conversion over increasing power and spectral ranges and they are also needed for higher average power nonlinear optical frequency conversion applications of remote detection and communication over long distances through the atmosphere. The potential of such applications have provided motivation for research in nonlinear optics for many years. We are now witnessing the advances that allow many of these applications to be realized.

III. Scientific Personnel Supported by this Contract

Principal Investigators

Professor Robert L. Byer	Applied Physics Department
Professor Robert S. Feigelson	Center for Materials Research

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Martin M. Fejer	Assistant Professor	Applied Physics
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Robert J. Raymakers	Crystal Grower	Center for Materials Research

Students and Degrees Awarded

C. David Nabors, Applied Physics, Ph.D., 1989

Gregory A. Magel, Electrical Engineering, Ph.D. 1990

Robert C. Eckardt, Applied Physics, Ph.D. 1991

Sung-Joo Ben Yoo, Electrical Engineering, Ph.D., 1991

Deiter H. Jundt, Applied Physics, Ph.D., 1991

Leslie Gordon, Applied Physics

N. H. Kim, Materials Science and Engineering

IV. List of all Publications Supported by
ARO Contract DAAL03-88-K-0113

1. W. J. Kozlovsky, C. D. Nabors and R. L. Byer, "Efficient second harmonic generation of a diode-laser-pumped cw Nd:YAG laser using monolithic $MgO:LiNbO_3$ external resonant cavities," IEEE J. Quantum Electron. **24**, pp. 913-919 (1988).

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