SINGLE CRYSTAL FILMS AND WAVEGUIDES OF ORGANIC MATERIALS; PREPARATION AND NONLINEAR OPTICAL PROPERTIES (F49620-96-1-0063)

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Final Report

The objectives of this program include: i) establishment of a method for the growth of thin single crystal films of important organic nonlinear optical materials, ii) detailed chemical and physical characterization of the films and iii) measurement of the nonlinear optical properties. We have successfully prepared single crystal thin films of several organic second order optical materials that include COANP, NPP, PNP, ABP, DAST and SPCD. These films were prepared using specific growth conditions following a method ("shear method"), invented by the principal investigator. This is the first time single crystal films of organic second order optical materials have been prepared. The areas of the films for COANP, NPP, PNP and ABP were large (>2 cm^2). For DAST the film-area was small ~20mm^2. The primary reason for the smaller area of DAST film was found to be its significantly lower solubility at ambient temperature and pressure.

The films of NPP, COANP, PNP and ABP have been characterized in detail by polarized optical microscopy, FTIR, optical absorption spectroscopy and x-ray diffraction. The studies have clearly elucidated the influence of polar interaction and predictability of molecular orientation in the shear-grown films. For example, both NPP and PNP molecules were found to organize along the substrate surface since the polar group was oriented sidewise with respect to the chromophore axis. In contrast, COANP molecules, having polar group along the molecular dipole axis, were oriented close to perpendicular to the substrate surface.

Detailed nonlinear optical measurements using second harmonic generation on the single crystal films have been completed for films of PNP and ABP. Measurements on NPP and COANP films were reported previously. The measurements have shown very large second order susceptibilities for the films. For example, the magnitude of d_{21} of NPP is 97pm/V which is about 18 times that of the phase-matchable d-coefficient of $LiNbO_3$. The magnitude of d_{22} of COANP is 56pm/V. These magnitudes are extremely large and the films can be used for autocorrelation measurements in diagnostics of ultrashort laser pulses. A measurement of the d-coefficients can provide a reasonable estimate of the electro-optic coefficients. The correlation between the d-

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14. ABSTRACT
The objectives of this program include: i) establishment of a mehtod for the growth of thin single crystal films of important organic nonlinear optical materials, ii) detailed chemical and physical characterization of the films and iii) measurement of the nonlinear optical properties. We have successfully accomplished these goals for several important organic materials. We have prepared and characterized single crystal films. The films of several materials have shown exceptionally large nonlinear optical and electro-optic coefficients. We expect a wide range of applications in photonics using such films.

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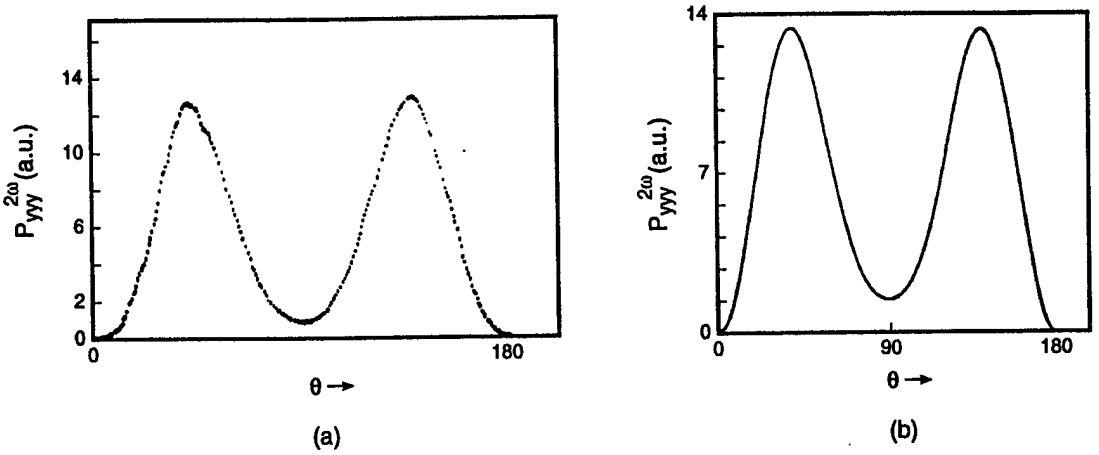
coefficient and electro-optic coefficient is: $r_{ijk} = - 4d_{ijk}/(n_{ii}n_{jj})^2$. The d-tensor elements of the films were measured by second harmonic generation under various polarization conditions and with sample rotation. The results for a specific polarization condition, for a PNP sample (film orientation, [101]) is given in the following.



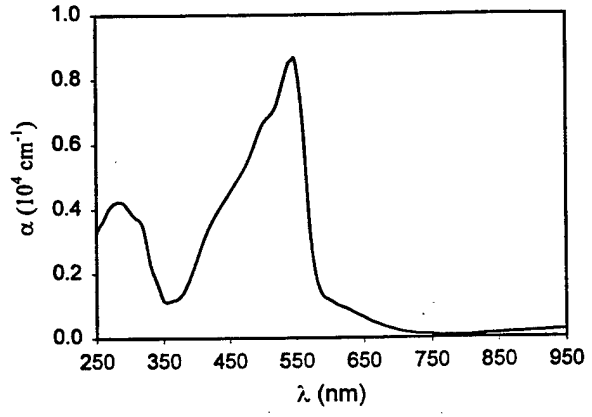
a) Measured second harmonic power, $P_{yyy}^{2\omega}$ for a PNP film as a function of angle of rotation of the film around the beam propagation direction. The input and output polarizations are parallel to each other.

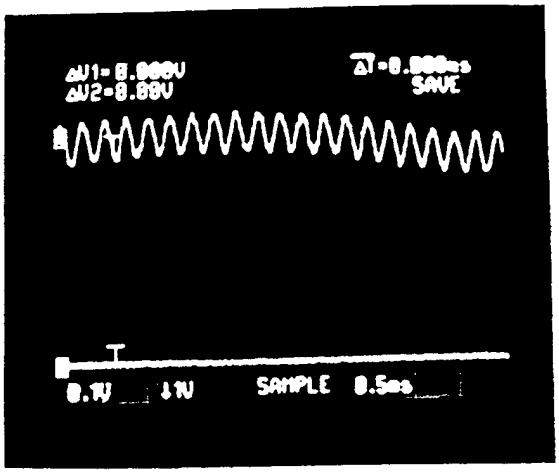
b) Calculated second harmonic power as a function of angle of rotation.

For PNP, the magnitude of d_{21} was 65 (±5) pm/V and the ratio d_{21}/d_{22} was equal to 2.5. This measurement technique has provided both sign and magnitudes of the second order tensor elements of the films.

We have recently reported electro-optic measurement on DAST films in the transverse configuration. A Ti:Sapphire laser was used for this measurement. The measurement was made using Mach-Zehnder interferometry and also by field-induced birefringence measurement in the cross-polarized configuration. Gold electrodes were deposited on the film to apply electric field in the transverse direction along the a-axis which lies on the film plane. The film with the electrodes was placed in one arm of the Mach-Zehnder interferometer to introduce phase changes using electric field while in the other arm light traveled through air. The laser light polarized parallel to the dipole axis (a-axis) was transmitted through the DAST film of thickness 3μm. One of the corner mirrors of the Mach-Zehnder interferometer was attached to a piezoelectric drive to control the bias point in the Mach-Zehnder fringes. Light modulation at an optimum bias point was measured for different magnitudes of applied electric field using a photodiode and recorded using lock-in detection. At about 720 nm where absorption is small the measured phase change was extremely large and

therefore the intensity modulation was very large as detected using an oscilloscope. A modulation of 20% was observed for a field of 1V/μm at 4kHz (film thickness ~ 3μm). The oscilloscope trace of the modulation signal for the field at 4 kHz is shown in the following. Clearly, the observed modulation is large for a thin film sample and this result provides the demonstration of a thin-film single-pass electro-optic modulator. The magnitude of r_{11} at 720nm is 530pm/V. Considering the reported d-coefficient of DAST (1900pm/V at 1200nm), such a high electro-optic coefficient can be expected. Speeds many orders of magnitude higher than 4kHz, of-course, is expected and have been demonstrated for materials such as this. Therefore, the potential for applications of these films is significant. The geometry involving the field-induced birefringence is directly relevant to actual devices.





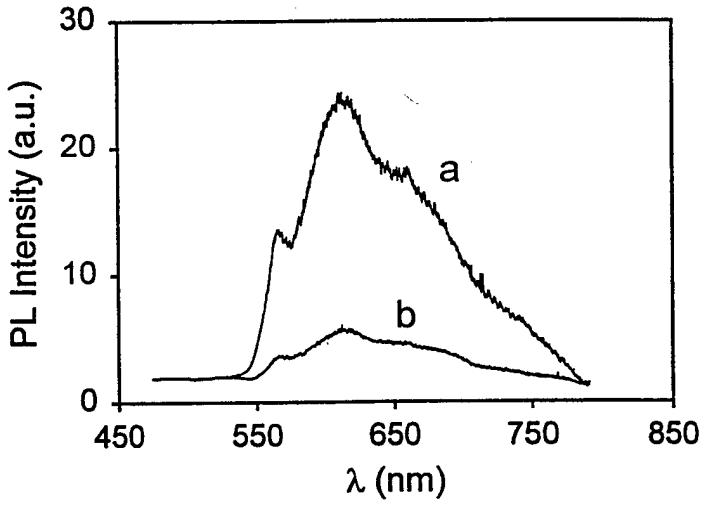
a) The figure on the left gives the absorption spectrum of a DAST film.
b) The figure on the right shows the oscilloscope trace for electro-optic modulation with about 20% modulation depth as measured for a thin-film of DAST. The measurement was made by field induced birefringence under cross-polarized condition at an optimum bias point. The applied field was 1V/μm at 4kHz.

Electro-optic modulation in a Fabry-Perot cavity containing a NPP film has been demonstrated. Channel waveguides were directly fabricated for NPP through growth on a patterned substrate. The guides thus obtained were characterized for electro-optic modulation and a large modulation was observed for a 3mm long guide applying 20V d.c.

The off-resonant nonlinear refractive index has been measured for PTS-polydiacetylene crystal using z-scan and Michelson interferometry. The sign was unequivocally negative and the magnitude was (10^{-5} cm^2/MW) consistent with previous reports. This result clearly shows that

bleaching of the exciton absorption has the dominant contribution to the optical nonlinearity of PTS-polydiacetylene. Significant spectral broadening due to self-phase modulation (off-resonant nonlinear refractive index) was observed in a PTS-polydiacetylene crystal using 2ps pulses at low intensities. This result shows promise for using this material for pulse compression application. Picosecond all-optical switching with 50% modulation depth was previously demonstrated in the Fabry-Perot geometry at 1.06μm.

We have observed strong polarization dependent photoluminescence in both phases of DAST single crystal films for excitation at 400nm with 2ps pulses from a Ti:Sapphire laser. The photoluminescence peaks appeared at 610nm for the red phase (noncentrosymmetric) and at 585nm for the orange phase (centrosymmetric). These results are promising for potential applications of the films in LEDs and lasers.



The photoluminescence spectra of DAST (red phase) for: a) incident polarization parallel to the dipole axis and b) incident polarization perpendicular to the dipole axis.

Thus, as these results show, we have made significant progress in both growth of single crystal films as well as nonlinear optical measurements of several important organic materials. In the future, we intend to make substantial improvement in the thin-film crystal growth of some of the key organic materials such as the stilbazolium salts and specific other materials and make detailed nonlinear optical measurements on the single crystal films over a wide range of wavelengths. We will also fabricate specific device structures using these films.

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