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Investigation of Organic Nonlinear Optical Crystals for Harmonic Frequency Conversion and Electro-optics

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Executive Summary

This is a final report of the Department of Energy, Grant No. DE-FG03-96SF21142 entitled, "Investigation of Organic Nonlinear Optical Crystals for Harmonic Frequency Conversion and Electro-optics". Dr. Ravindra B. Lal, Professor of Physics is the principal investigator of this grant. The research performed under this grant is through the Research Collaboration Program for Historically Black Colleges and Universities under the overall directions of Dr. Kennedy Reed of Lawrence Livermore National Laboratory (LLNL), Livermore, CA. The technical collaborator for this research is Dr. Howard W.H. Lee of LLNL.

We are conducting a detailed study of the crystal growth of different organic materials and their physical, optical and morphological properties. The crystals are grown by a novel solution crystal growth technique developed by the principal investigator at Alabama A&M University (AAMU). Our studies included the measurement of solubility of organic NLO materials in different solvents, growth of crystals by solution growth technique, and the characterization of optical properties and damage threshold of crystals for high power laser applications. Two different NLO crystals of 4-Aminobenzophenone (ABP) and 3-methoxy-4-hydroxy-benzaldehyde (MHBA) were investigated during the course of this investigation. A paper on ABP crystals was published in Journal of Crystal Growth in 1997 [1].

The work is further extended under a subcontract B336498 from University of California, Lawrence Livermore National Laboratory, Livermore, CA.
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1.0 Introduction

The development of organic materials for use in nonlinear optical (NLO) devices is of interest because their optical nonlinearities are orders of magnitude higher than their conventional inorganic counterparts like, lithium niobate (LiNbO3) and potassium dihydrogen phosphate (KDP). Many organic materials have also emerged as a leading choice for optoelectronic and photonic applications. We are conducting a detailed study of the crystal growth of different organic materials and their physical, optical and morphological properties. The crystals are grown by a novel solution crystal growth technique developed by the principal investigator at Alabama A&M University (AAMU). Our studies included the measurement of solubility of organic NLO materials in different solvents, growth of crystals by solution growth technique, and the characterization of optical properties and damage threshold of crystals for high power laser applications.

1.1 Objectives:

Our research involves the development of new organic materials for applications in nonlinear optics, optoelectronics and photonics, and sensors. Specifically, we intend to:

- Develop, synthesize, and grow new organic-based organic materials with high optical nonlinearities.
- Investigate and characterize the optical properties of these crystals.

1.2 Background and Importance of the Project

Green and blue lasers are of far reaching importance to applications in optoelectronics such as high-density optical memories, color displays, etc.
NLO organic crystals are playing a very important role in generating green and blue laser beams. In recent years considerable effort has been expended in search of organic crystals for NLO applications.

4-Aminobenzophenone (ABP) and 3-methoxy-4-hydroxy-benzaldehyde (MHBA) are relatively new organic NLO compounds. The structure of ABP was reported by single crystal X-ray diffraction [2] ABP belongs to the monoclinic point group symmetry 2 and the space group P2₁, \( Z=2, a=12.036 \ A, b= 5.450 \ A, c= 8.299 \ A, \beta =97.86^\circ \), chemical formula \((C_6H_5)CO(C_6H_4NH_2)\), density =1.215 g/cm\(^3\), melting point =125 °C. The useful transmission range of ABP extends from 420 nm to 1400 nm, and its powder SHG efficiency is 360 times of ADP [3]. Therefore, single crystals of ABP are promising for generating green and blue laser beams from Nd:YAG or semiconductor diode laser. The crystal structure of MHBA is monoclinic with space group P2₁, point group 2 and the following cell parameters: \( a=14.057 \ A, b= 7.875 \ A, c= 15.037, \text{ and } \beta= 115.45^\circ \), density = 1.34 g/cm\(^3\). The transmission range of MHBA extends from 370 nm to 1600 nm. Its powder SHG efficiency is 30 times of urea. Therefore, the single crystals of MHBA are promising for blue and green laser generation.

2.0 Experimental Work

2.1 Purification of organic materials

Crystal growth of organic materials is extremely susceptible to the purity of the starting material. Commercially available organic compounds are generally of low purity and therefore, need to be purified to make them suitable for crystal growth purposes. Commercially obtained materials were purified by repeated crystallization in the proper solvents. Normally all compounds were recrystallized three times. The purity was tested by measuring the melting point of the material.

2.2 Determination of solubility in different solvents

For solution crystal growth of any material, it is necessary to
determine the solubility of the organic material in appropriate solvent as a function of temperature. The solubility of the chosen organic material was determined in different solvents and combination of solvents. A specially designed double jacketed flask with a capacity of 100ml was used for this purpose. The temperature of the solution was kept constant using a temperature controlled bath with an accuracy of ±0.01°C. The temperature of the solution was measured with a NBS calibrated thermometer with an accuracy of ±0.1°C and the solution was stirred with a magnetic stirrer. Small amounts of the organic material was added to the flask till all the material is completely dissolved at the required temperature. The solubility was determined between 30-50°C for each organic material in terms of gm/100ml of the solvent. It is important that the system is air tight to avoid any evaporation of the organic solvent. The key to solution crystal growth is the proper choice of solvent for growing crystals of desired morphology.

2.3 Solution Crystal Growth

The low temperature solution growth apparatus was modified to grow organic crystals using organic solvents [4]. The schematic diagram of this modified solution growth crystallizer is given in Figure 1. The main features of this crystallizer are: (i) better temperature stability even with sudden fluctuations in room temperature, (ii) better control over evaporation of organic solvents, (iii) a mechanical screw type arrangement for pulling the seed crystal at a controlled rate, and (iv) a possibility of varying the seed orientation and type. Better temperature stability was achieved by placing another glass container inside the double-walled jacketed vessel. The growth temperature was maintained at a temperature of ±0.01°C using constant temperature bath. The seed crystal is rotated clockwise and then counter-clockwise using an electronic reciprocating system. An air gap between the two glass walls provide an extra insulation for temperature stability. Moreover, spontaneous nucleation at the bottom of the growth vessel, which hampers the growth and the crystal yield, was eliminated by better temperature stability and insulation. By providing an extra lid on the
Figure 1

Modified reciprocating solution crystal growth crystallizer
inside glass vessel and a Teflon seal over the jacketed vessel, the evaporation of the solvent was reduced drastically. In a normal growth run the inner vessel is filled halfway with growth solution rather than three-fourth as in usual way. The grown crystal is pulled at a controlled rate and the supersaturation is created by reducing the growth temperature at a programmed rate from 0.01°C/day to 0.1°C/day during the entire growth period. Large and good optical quality crystals were grown by this technique.

2.4 Optical Characterization of Crystals

Optical absorption spectroscopy was performed at LLNL to determine the spectral range of absorption arising from impurities in the grown crystals. This will also determine the useful operating range of the crystals for harmonic frequency generation and electro-optics. Second harmonic generation on single crystals and powder samples is done to compare the optical nonlinearities of grown crystals with those of well characterized KDP crystals.

3.0 Crystal growth of ABP and MHBA

ABP crystals were grown at AAMU using low temperature solution crystal growth. The commercial ABP with a purity of 98% was purified by recrystallization several times in solvents such as acetone, toluene, or ethyl alcohol until the crystallites are bright yellowish in color. The solubility of ABP was determined in different solvents (Fig. 2). Ethanol gave a desirable yield for crystal growth. Because the growth of ABP crystals can easily lead to spurious nucleation, the perfection of seed crystals is very important for growing good crystals. The seeds must be without any macroscopic defects such as flaws and inclusions because it may cause spurious crystallization in solution. The crystals were grown from saturated solution by a novel solution crystal growth technique developed by the authors [4]. In this technique the seed crystal is pulled at a controlled rate equal to the growth rate of the crystal along with programmed cooling of the growth solution to
Figure 2
Solubility of ABP in different solvents

1- acetone; 2- mixture of acetone(A): toluene(T) in volume ratio 2:1;  
3- A:T = 1:1.4; 4- A:T = 1:1.2; 5- ethanol; 6- toluene
create a desired supersaturation. In this way, not only the crystal is annealed in-situ but also spurious aloevera-tree like growth of the seed is greatly reduced or completely eliminated. During the growth process, the seed holder was rotated with a rate of 30 rpm, and the solution temperature was decreased in 0.05-0.1°C per day. In our experiments the morphology of grown crystals was not affected by the solvent sources. The growth rate in the $b$ direction is higher than in the $a$ direction and much higher than in the $c$ direction. Crystals with good quality were successfully grown with the solvents such as, acetone, ethanol, and mixture of acetone and toluene. The largest crystal in size (18x25x12 mm$^3$) was grown with the solvent of ethanol in two weeks. The ABP single crystals have good chemical stability and are not susceptible to humidity. A copy of the paper published in the Journal of Crystal Growth is enclosed in the appendix.

The commercial material MHBA (impurity of 98% from Aldrich Chemical Company) was purified by recrystallization several times in solvents such as methanol or ethyl alcohol. Solubility of MHBA was measured in different solvents and is given in Fig. 3. Single crystals of MHBA were grown from a mixed solution of methanol and ionized water by low temperature modified solution crystal growth technique [4]. The largest crystal in size (60x30x5 mm$^3$) was grown with solvent of ethanol in two weeks. The work on MHBA crystals is continued under the subcontract from LLNL. A crystal grown in this project will be examined by optical techniques at LLNL in collaboration with Dr. Howard Lee.

4.0 Characterization of the grown crystals

Optical data on ABP crystal was taken at the Photonics Group, Lawrence Livermore National Laboratory. Optical absorption data was taken using CARY 5 UV-VIS-NIR dual-beam spectrophotometer between 400-1500 nm. Frequency doubling measurements were made using a Nd:YAG laser and a Ti:Sapphire regenerative amplifier operating at approximately 150 fs and 0.7 mJ/pulse. Three wavelengths (850, 950, and 1064 nm) were selected from a white continuum generated by focusing the
Solubility of MHBA in Different Solvents

Figure 3
output of the regenerative amplifier onto a 0.25" thick fused silica substrate with bandpass filters. The result of optical absorption for ABP crystal is shown in Fig. 4. The useful transmission range of ABP single crystals extends from 420 to 1400 nm. ABP crystal gave SHG efficiency of approximately 10%. Higher efficiencies are expected to be achieved by optimizing the phase-matching orientation, improving crystal polish, and optimally coupling the incident power into the crystal. ABP single crystals could be a promising material for generating green and blue laser beams.

Measurement of laser damage threshold for ABP crystal was conducted at the above indicated wavelengths by observing differential scatter from a He-Ne laser [5]. The result of this measurement gave a damage threshold value of 1-2 GW/cm2. These values are comparable to those for inorganic crystals and dispel the misconception that organic crystals are susceptible to extensive laser damage.

5.0 References


6.0 Acknowledgments

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Appendix