Growth and characteristics of Schiff base organic nonlinear optical crystals

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The synthesis and crystal growth of a new organic nonlinear optical material, a Schiff base compound, 4-nitrobenzylidene-4-chloroaniline is reported. Good-quality crystals have been successfully grown using Bridgman-Stockbarger technique. The synthesized material has been characterized via Fourier transform infrared (FTIR) spectroscopy and DSC studies. Nonlinear optical activity of the organic crystal, 4-nitrobenzylidene-4-chloroaniline, shows good second harmonic generation of 1.064 micron wavelength.

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1. Introduction

Nonlinear optical (NLO) materials capable of generating the second harmonic frequency play an important role in the domain of optoelectronics and photonics [1-3]. Nonlinear optical crystals with high conversion efficiencies for second harmonic generation (SHG) and transparent in visible and ultraviolet ranges are required for numerous device applications. The NLO materials which provide the active medium for nonlinear processes can be divided in three broad categories: (i) Molecular materials such as organic systems in which chemically bonded molecular units interact in the bulk through weak van der Waals forces. Optical nonlinearities in these systems are often considered to be primary; (ii) Covalent and ionic systems consisting of mainly inorganic ionic crystals and semiconductors; and (iii) semi-organic materials. The tremendous advantages offered by organic NLO materials are the high nonlinear figure-of-merit (FOM) for frequency conversion, high laser damage threshold and fast optical response time together with the flexibility of molecular structures and confirmations as well as their adaptability to various device structures such as films and fibers.

In this paper, the successful growth of new large size NLO crystals of the Schiff base [4-7] compound: 4-nitrobenzylidene-4-chloroaniline was accomplished by modifying the growth apparatus or technique. Crystal growth results and certain physical property measurements are presented herein.

2. Experimental

2.1 Synthesis of Schiff base compound: 4-nitrobenzylidene-4-chloroaniline

The chemicals required (4-nitro benzaldehyde; 98% and the.4-chloroaniline; 98% purity) for the synthesis was purchased from the Aldrich Chemical Company, Milwaukee, Wisconsin, USA. The Schiff base compound, 4-nitrobenzylidene-4-chloroaniline, was prepared by refluxing equimolar quantities of 4-nitrobenzaldehyde and the corresponding aniline in ethanolic solution for about an hour, according to the reaction illustrated in Fig. 1.:

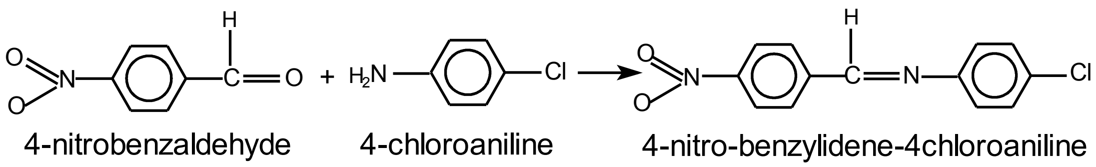

Fig. 1. Reaction for the synthesis of the compound 4-nitrobenzylidene 4-chloroaniline.

On cooling, the crystals of the compound appeared. These crystals were separated and re-crystallized from ethanol.

The compounds crystallized out as pale yellow crystallites.

2.2 Growth of crystals by Bridgman-Stockbarger (BS) technique

In this technique, the sample is encapsulated in a sealed tube, placed in a hot zone (above the melting point) of the furnace, and slowly lowered into the cold zone below the melting point. The molten sample solidifies as it moves into the cooler part of the furnace. The materials suitable for growth by this method are those compounds which are thermally stable. In order to obtain good quality crystals usually a translation rate has to be determined for each crystal such that compensation for super cooling tendencies and poor thermal conductivities are achieved. The BS system consists of two separate temperature zones, growth chamber, ampoule lowering arrangement and temperature controllers. It consists of an Acme-type lead screw with a pitch of six threads per inch.

This is threaded with a nut which is attached to a flat aluminum plate and a spur gear. A timing belt that is attached to another idling assembly which is rotated by a belt driven by a stepper motor rotates this gear. This arrangement is attached to a conical tip, and 15 cm long Pyrex ampoule, containing material to be grown. The furnace is supported by a vertical stand that consists of upper and lower aluminum plates connected by 25 cm long screws threaded at both ends. Each of the two zones of the modified BS furnace consists of circular 10 cm diameter tubes, ground and rough polished on both sides, that are sandwiched between two machined aluminum flanges using specially molded "O"-ring seals and RTV two-part rubber adhesive. The length of the hot zone is 5cm and the cold zone is 17.5 cm.

A Teflon insulation plate separates the zones. The centers of the insulation plate, top plate of the vertical stand, top and bottom of the upper zone, and top of the lower zone has 2.5 cm diameter holes through which a 2.5 cm diameter tube closed at one end is placed and sealed to the flanges using silicone "O"-rings. During the crystal growth process the ampoule is lowered through a temperature gradient as it moves through this tube from the hot zone to the cold zone. The hot and cold zones of the furnace are fitted with inlet and outlet tubes for connection to Neslab circulating baths that provide thermal stability to ±0.1 °C. Fig. 2 shows photograph of the actual system designed and fabricated in our laboratories with all the requisite accessories respectively. The details of the system are given elsewhere [8-9]. For each run the ampoule was filled with the sample and hung from the glass pulling rod and the hot zone and cold zone temperatures are gradually increased until the entire solid melts. The hot zone is kept at a few degrees above the melting point. Then the temperature of the cold zone is gradually lowered till a small seed has formed at the tip. Once the seed is formed the sample is rotated and lowered at the same time, at a rate of 0.01 to 0.04 cm h^{-1}. The grown crystals are cut to about 2 mm thick perpendicular to the growth direction. Hand polishing of crystals was done with various sizes of alumina powder starting with 100 µm and ending with 0.05µm. Each powder is mixed with white petrolactum and the crystals polished using clockwise and anticlockwise circulatory motion. A polishing cloth in the final step is used to remove the excess of polishing powder and possible moisture contents.

Fig. 2. A photograph of modified Bridgman Stockbarger (BS) set-up.

2.3 Characterization of the grown crystals

The melting point of the grown crystals was determined using a differential scanning calorimeter (Perkin- Elmer DSC-4). A small piece of the grown crystal is sealed in the DSC cell then the measurement is determined using a heating rate of 10ºC /min for each sample. The infrared spectra of each of the melt grown were recorded using the polished crystals on a Nicolet Avatar instrument. The grown crystals have been tested for the second harmonic generation using a Q –switched Nd: YAG laser (continuum) with a repetition rate of 10Hz in the laboratory.

3. Results and discussion

Good quality and large crystals have grown by Bridgman-Stockbarger (BS) Technique. Fig. 3 shows the photograph of a grown crystal. In DSC studies, during the heating cycle, no phase transition was observed for any sample. Powder samples of the materials and grown crystals give the same value for melting points. Only noticeable change is the intensity of color for grown materials which are seen to have a deeper hue, most probably the effect due to thermo-chromic effect. The grown crystals are found to be very stable chemically under normal conditions showing no decomposition. The onset temperature indicates the melting point. The melting point was found to be around 132 ºC. The FTIR spectra of 4-nitrobenzylidene 4-chloroaniline I shown in Fig. 4. The Analysis of fingerprint region of IR spectra of the described in Table 1.

Fig.3. A Photograph of the melt grown crystal .

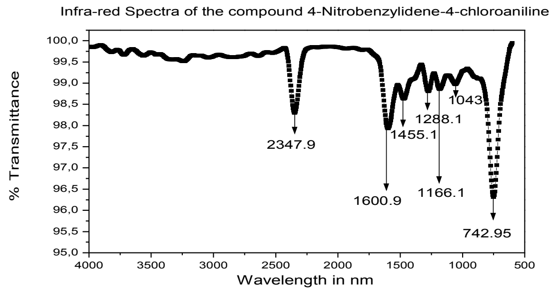

Fig. 4. FTIR spectrum of single crystal of 4-nitrobenzylidene 4-chloroaniline.

Table 1. Analysis of the fingerprint region of IR spectrum of the melt grown crystal: 4-nitrobenyzlidene-4-chloroaniline.

Group	**Found in cm^{-1}**	**Expected in cm^{-1}**
-C=N-	1600.9 (s)	1620(s)
Aromatic C-C- multiple bond	1455.1	~1450
-C-H bend	1288 1166.1	1269-1247(w) 1183-1171 (w)
C-Cl (stretch)	742.95 (s)	830-600 (s)

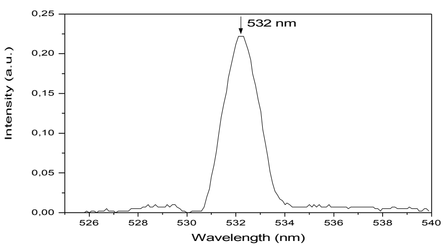

Fig. 5. Spectrum of the light scattered from the crystal of 4-nitro-4 chlorobenzylidene aniline crystal when illuminated with IR radiation of 1.064 micron wavelength.

The results of nonlinear optical characterization for second harmonic generation are presented in Fig. 5. Fig.5 shows the spectrum of the light scattered from the sample when illuminated with IR radiation of 1.064-micron wavelength. The peak wavelength of the spectrum is 532 nm, which is the second harmonic of the input IR radiation. The crystal, 4-nitro-4 chlorobenzylidene aniline, exhibits optical nonlinearity the second order and can be potentially used as a material for second harmonic generation.

4. Conclusions

The important experimental results of our investigations can be summarized as follows:

The new derivative of Schiff base compound, 4-nitro-4 chlorobenzylidene aniline has been successfully synthesized and large sized crystals have been grown by modified Bridgman technique. The grown crystal shows no phase transition, and is extremely stable in air. The crystal exhibits optical nonlinearity of the second order and can be potentially used as a material for second harmonic generation.

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