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Growth and characterization of an organic nonlinear optical crystal: Benzilic Acid

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ABSTRACT

Benzilic Acid is an organic material with interesting nonlinear optical properties, in particular Second Harmonic Generation (SHG).It was synthesized and single crystals were grown by slow evaporation method. Unit cell parameters were evaluated by single crystal and powder X-ray diffraction techniques. The formation of the material was confirmed qualitatively by FT-IR analysis and its optical transmittance was studied. The Thermal and mechanical properties were analised. The SHG efficiency was also measured.

Introduction

During the past two decades, formidable attempts have been devoted to the synthesis and crystal growth of new compounds for potential applications in nonlinear optics.

As a result , a variety of both organic and inorganic materials have been developed [1-3]. In recent years ,organic crystals are rated high as compared to inorganics in view of their large electro-optic effects with low frequency dispersion, low cost, fast and large nonlinear response over a broad frequency range, inherent synthetic flexibility and intrinsic tailorability [4,5].

High-quality organic NLO crystals must posses sufficiently large NLO coefficient, transparent in UV region, high laser damage threshold power, and easy growth with large dimensions[6-9]. Some of the other advantages of organic materials are the scope for altering the properties by functional substitutions, high degree of nonlinearlity and high damage resistance. However their practical applications are limited by poor phase matching properties caused by large stacking of the structure and other factor.

Owing to the high polar nature of the molecules , they often tend to crystallize as long needles or thin platelets[10,11]. For optimization of second order nonlinearities in organic molecular crystals two properties are particularly important in addition to noncentrosymmetry i.e., strong π electron delocalization and intermolecular charge transfer stimulated by the presence of electron donor and acceptor groups.

A particularly well-suited class molecules is the di-substituted benzene in which an electron donor and electron acceptor are substituted from opposite sides of a benzene ring [12]. Because of its sensitivity to the crystal symmetry, the second order susceptibility can provide valuable information about structural changes in noncentrosymmetric materials[13].

Up to now ,several hundreds of donor and acceptor substituted delocalized π electron systems have been reported with enhanced nonlinear optical properties. But, only a few of them could be used in possible applications like modulators ,SHG and optical waveguides owing to difficulties in getting transparent good quality and considerably large size crystals. In this paper, we report the synthesis, crystal growth and characterization of the organic NLO material Benzilic Acid.

The crystal structure of benzilic acid(C14H12O3), as reported previously by YongcaiQiuetal [14], is orthorhombic (spacegroup Pna21). In the present investigation, we have grown benzilic acid crystals by the slow evaporation technique as suggested by YongcaiQiuetal.

The grown single crystals have been subjected to various characterization studies such as single-crystal X-ray diffraction(XRD), powderXRD, FTIR, UV–vis, thermal SHG.

Experimental

Crystal growth

The slow evaporation technique is widely used for the growth of organic crystals to get more transparent single crystals.

The single crystals of benzilic acid were successfully grown by slow evaporation solution growth technique at room temperature using ethanol as solvent.

The commercially available benzilic acid was taken as the raw material for the growth of the crystals. Since benzilic acid is insoluble in water, ethanol was chosen as the solvent for our growth.

The saturated solution of benzilic acid was obtained by dissolving the charge material in ethanol and continuous stirring of the solution using a Magnetic stirrer at room temperature. After reaching saturation the solution was filtered and the beaker containing the solution was optimally closed for controlled evaporation. Transparent single crystals were obtained from mother solution after 15 days (Fig. 1).

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Fig(1)-Benzilic Acid single Crystals

Molecular Structure

Figure (2) illustrates the molecular structure of benzilic acid single crystal

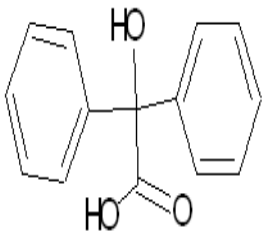


Fig (2)- Molecular Structure-

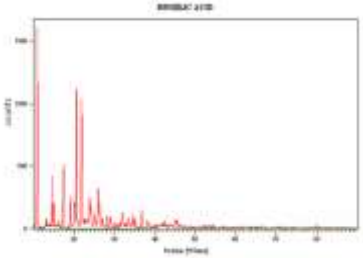
Characterization:

The Grown single crystals of benzilic acid have been analyzed by different characterization techniques. The crystals were confirmed by single crystal X-ray diffraction analysis using ENRAF NONIUS CAD4 diffractometer. The functional groups were identified by using PERKIN ELMER RX1 Fourier Transform Infrared spectrophotometer in the range of 400-4000 cm-1. The optical properties of the crystals were examined between 200 and 1200 nm using LAMBDA-35 UV-Vis spectrometer. The mechanical and thermal property of the grown crystals have been analysed. The NLO efficiency of the grown crystals were also studied.

X-ray diffraction Analysis

Single-crystal XRD analysis confirms that the grown benzilic acid crystal belong sto the orthorhombic system with the space group Pna21 and the lattice parameters are a = 11.277(3)A°, b = 8.654(5) A°, c = 24.417(2) A°, $\alpha = \beta = \gamma = 90°$. These values are in good agreement with the reported values [14].

This has been confirmed by powder XRD diffraction analysis by using a Rich Seifert diffractometer with $C_uK_\alpha(\lambda=1.5417A°)$ radiation. The powder XRD pattern of benzilic acid crystal is shown in fig 3. The orthorhombic structure of the grown crystals have been confirmed and Table. 2 gives the d-spacing & their respective indices. The well defined peaks at specific 2θ values show high crystallinity of the grown crystals. This work was indexed using the TREOR software package following the procedure of Lipson and Steeple[15]. Also UNIT CELL software package was used to confirm the indexing.



Figure(3) – Powder XRD Pattern of Benzilic Acid Crystals

FTIR analysis:

The Fourier Transform Infrared spectroscopy is effectively used to identify the functional groups present in the synthesized compounds. FTIR measurement was carried out in the range of 400-4000 cm-1 using the PERKIN ELMER RX1 Fourier Transform Infrared spectrometer prepared by mixing powdered Benzilic Acid Crystals with KBr pellet technique is shown in Figure 4. For organic molecule, the FTIR region has been divided into fractional group and fingerprint region. The fractional group region extends from 4000 cm-1 to 1300 cm-1, whereas fingerprint region are those lying between 1340 to 900 cm-1.The spectrum shows the symmetric and asymmetric stretching modes of free NH_2 group, which are observed at 3051 and 2638.81 cm-1. The peaks at 2534.76 cm-1 may be assigned to overtone of bonds due to 1307 and 1201 cm-1. The vibration between 913.07 and 633.58 cm-1 are usually associated with the presence of the benzene rings in the Benzilic Acid Crystal molecule. The peaks at 799.27 cm^{-1} show the meta position of the substituted molecules in the benzene ring of Benzilic Acid Crystals [16]. The peaks that appear at 1418 cm-1 are due to the vibrations of NO_2 stretching modes which are not much broad, their interaction with the neighbouring molecules are presumed to be weak bonds. Nevertheless, the dipole-dipole interaction between the dominating forces in the packing of molecules in the crystal lattice.

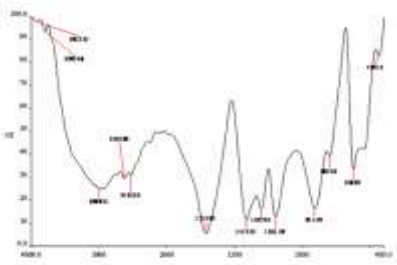


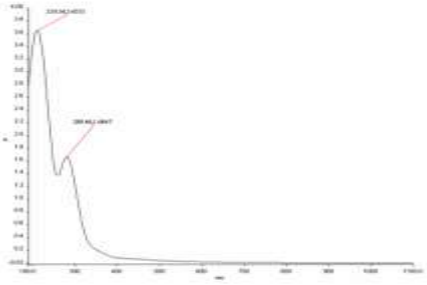
Figure (4) – FTIR Spectrum of Benzilic Acid Crystals

UV–visible spectral analysis

For optical applications especially for SHG, the material considered must be transparent in the wavelength region of interest. .The UV-VIS spectral analysis has been carried out using LAMBDA-35 UV-Vis spectrophotometer in the wavelength range of 200 – 1200 nm. Transmission spectra are very important for any NLO material because a nonlinear optical material can be of practical use only if it has wide transparency window. To find the transmission range of the sample, optical transmission spectrum was recorded as shown in Figure(5) ,which gives information about the structure of the molecule, because the absorption of UV and visible light involves promotion of the electron in the s and p orbital from the ground state to higher states[17]

The transmittance is found to be maximum in the entire visible and infrared regions. When we consider the percentage of transmission we observe that the transmission has been increased much in the visible region. From the spectrum it is observed that the crystal shows a good transmittance in the entire visible region.

The lower cutoff at 280 nm attest the usefulness of this material for optoelectronics applications and the second harmonic generation of the Nd:YAG laser [18] and for the generation of the higher harmonics of the laser diodes.



Figure(5) – UV –Visible Spectrum of Benzilic Acid

Thermal Analysis :

The thermal analysis (TGA) was carried out by using TAQ-500 analysier at a heating rate 25^0 / min for temperature range 50 to 900^o in nitrogen inert atmosphere to study the weight loss and thermal stability. The thermogram is shown in fig(6). It reveals that the major weight loss of about 62% takes place in the region 167.73^o C and 307^o C. This loss of weight may be due to the liberation of volatile substances. From the figure it is clear that the grown crystals are stable upto the temperature of 167.73^o C. There is no weight loss upto 100^o C, ensuring the absence of water in the crystal structure. Thus the grown crystal is a best suitable material for NLO application.

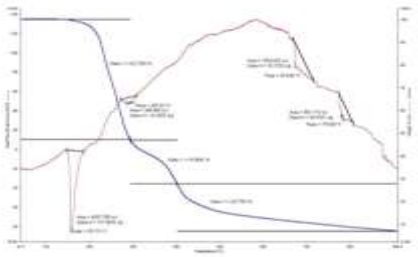
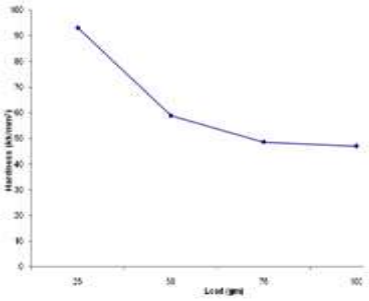


Figure (6)- TG-DTA Thermogram of Benzilic Acid Crystal

Vickers hardness test

The mechanical property of the benzilic acid single crystal has been studied using LEITZ microhardness tester . Vickers microhardness indentation test is used to characterize the hardness of the material. Measurement of hardness is a non-destructive testing method to determine the mechanical behavior of the materials .It is a resistance against plastic deformation .By definition the indentation hardness is the ratio of the applied load to the surface area generated due to indentation. A well polished Benzilic Acid crystal has been placed on the platform of Vickers micro hardness tester and the loads of different magnitudes have been applied in a fixed interval of time. The indentation time has been kept 10 seconds for all the loads. Vickers micro hardness values have been calculated by using the formula $Hv=1.8544 \times P/d^2$ Kg/mm^2. Where Hv is the Vickers micro hardness number, P is the applied load in Kg, d is the mean diagonal length of the indentation impression in mm and 1.8544 is a constant of a geometrical fraction for the diamond pyramid. The hardness values have been taken for various applied loads over a fixed interval of time. A graph has been plotted between hardness number (Hv) and applied load as shown in the figure7.At lower loads hardness decreases with much with load . At higher loads above 50 gm cracks begin to occur which may be due to the release of internal stresses generated locally by indentation[19].Hence it may be suggested that the material may be used for the device below the applied load of 50gm. The relation connecting the applied load(P) and diagonal length (d) of the indenter is given by the Meyer Law[20]. From Meyer's Law $P=ad^n$ connecting the applied load (P) and diagonal length (d) of the indentation, the work hardening coefficient 'n' was calculated. Here 'a' is a constant for a given material From the observations on various materials [21,22], it is pointed out that 'n' lies between 1 and 1.6 for hard materials and is greater than 1.6 for soft materials. Since the value of work hardening coefficient of the grown crystal is 1.1 it is considered to be a hard material.



Figure(7) Vickers Hardness Vs load for ZTC Crystals

Conversion efficiency:

The powdered sample was illuminated by the fundamental beam of 1064nm from Q-Switched Nd:YAG laser Prolab170 Quanta ray has been used to measure the SHG property of Benzilic Acid single crystal by the Kurtz and perry technique[23].The crystal has been ground into the fine powder and densely packed in between two transparent glass slides. Pulse energy of 4mJ/pulse and pulse width 8 ns with a repetition rate of 10Hz has been allowed to strike the sample cell. The SHG was confirmed by the emission of green radiation and the parent ray was filtered using an IR filter. The SHG output voltage was measured using a photomultiplier and a digitalizing oscilloscope assembly. The output voltage was found to be 160mV which is 2 times higher than KDP. Since the crystal has higher SHG efficiency than KDP it is a best suitable material for NLO applications.

Conclusion

Good optical quality single crystals of benzilic acid have been grown by solution growth method at room temperature. The lattice parameters have been found by single crystal X-ray diffraction technique. The FT-IR spectrum reveals the various functional groups present in the grown crystal. The optical absorption spectrum reveals that the crystal has wide optical window from 300nm to 1100 nm. The crystal is transparent in the visible and near infrared spectral regions. Optical transmittance of the crystal is high. The Vicker's microhardness was calculated in order to understand the mechanical stability of the grown crystals. Hardness measurement shows that the hardness of the sample crystals are appreciable. From the thermogram it is clear that the grown crystals are stable upto the temperature of 167.73^o C. The SHG output voltage was measured using a photomultiplier and a digitalizing oscilloscope assembly. The output voltage was found to be 160mV which is nearly 2 times higher than KDP.

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Table (1). X-ray powder diffraction data of Benzilic Acid crystals

θ	d-spacing [Å]	FWHM
10.8441	8.15878	0.1673
14.5181	6.10135	0.1004
14.9586	5.92261	0.2007
16.2832	5.44370	0.2676
17.3786	5.10296	0.1506
19.1902	4.62513	0.2676
20.1646	4.40377	0.1338
20.5984	4.31201	0.1673
21.8249	4.07239	0.1338
23.8549	3.73023	0.2342
24.1920	3.67900	0.2007
25.0296	3.55776	0.2676
25.8603	3.44533	0.1673
26.2734	3.39209	0.1673
27.0595	3.29530	0.2342
28.1704	3.16783	0.2676
28.9543	3.08382	0.4015
30.0929	2.96968	0.2007
31.2155	2.86541	0.2676
31.8963	2.80578	0.2676
33.3569	2.68619	0.2676
34.4445	2.60382	0.1338
35.0558	2.55981	0.2676
36.7361	2.44649	0.3011
38.0383	2.36568	0.3346
40.2183	2.24234	0.2676
45.1404	2.00861	0.8029
47.3758	1.91893	0.4015
48.7156	1.86924	0.4015