Studies on the Growth and Characterization of Zinc Phthalate Crystal

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Abstract: ***Semi organic non-linear optical crystal of zinc phthalate have been synthesized and grown successfully from aqueous solution by slow evaporation technique. The grown single crystal was characterized by different instrumentation techniques such as XRD, EDAX FT-IR, UV-Vis, photoluminescence and SHG test. The grown crystal was subjected to powder X-ray diffraction for analyzing the crystalline nature of the sample. The identification of ions in the crystal was done using the EDAX spectrum. FTIR studies reveal the functional groups and the optical characters were analyzed by UV-Vis spectral studies and PL studies. SHG efficiency of ZAP crystal was tested using Nd:YAG laser which confirms the NLO activity of the grown crystal.***

Keywords: Growth from solutions, X-ray diffraction, FT-IR, Optical transmission, Second harmonic generation, photoluminescence, EDAX

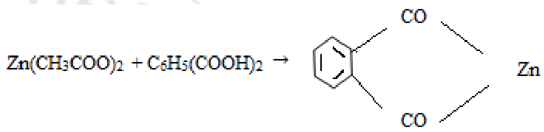
1. Introduction

NLO materials play an important role in the field of fiber optical communication, laser technology, optical signal processing and also opto-electronics, telecommunication, and optical storage devices due to their potential applications in emerging optoelectronic technologies [1-6]. In order to satisfy the day to day technological requirements, many scientists focussed their attention on the growth of materials which have a good nonlinear optical behaviour and be optically transparent in the visible and IR regions. Recent works showed that the organic crystals have been very large nonlinear susceptibilities than the inorganic one, but it has low laser damage threshold, inadequate transparency, poor optical quality, lack of robustness, inability to produce large crystals. In the case of inorganic NLO materials, through they have excellent mechanical and thermal properties, they have relatively modest optical linearity's due to the lack of extended π – electron delocalization [7, 8]. Hence in the several years research is focused on new types of NLO materials which combine the advantages of organic and inorganic materials called semi organic materials. Two types of semi organic material include organic and inorganic salts and metal organic coordination complexes [9-14]. Various studies of zinc phthalate crystals have been already reported [15-16]. Potassium acid phthalate [17], nickel phthalate [18] are the famous reported semi-organic phthalate crystals. In continuation of the above work, an attempt has been made to grow semi organic crystal and the characterization of these crystals have been investigated and reported in this work. The present work reports the growth and characterization of zinc phthalate, new semi organic crystal which have high optical quality.

2. Experimental Procedure

Synthesis and Crystal growth

The Zinc Phthalate crystal has been grown from aqueous solution by slow evaporation technique by dissolving a stoichiometric amount of high-purity phthalic acid and zinc acetate (merk) in double distilled water. The following reaction estimates the required quantity of Zinc Acetate and phthalic acid.



The synthesized salt was stirred in a magnetic stirrer at room temperature for 5 hours, in a water solvent to get homogenous mixture. The prepared solution was filtered by micro filter paper of 0.1µm porosity and kept in the dust-free atmosphere. Defect-free seed crystal was suspended in the mother solution, which was allowed to evaporate at ambient temperature. It has been observed that the solution containing phthalic acid and zinc acetate gave good bulk crystals, within the period of 4 weeks.

3. Characterization Techniques

3.1 Powder X-ray diffraction analysis

The powder X-ray diffraction analysis is useful for confirming and to identify the crystal and determining the phase purity of the sample. The grown sample was subjected to powder X-ray diffraction using DIMAX ULTIMA – III with 1.5406Å radiation and the collected data are presented in Table 1. The observed powder XRD pattern of zinc phthalate crystal is shown in Fig 1. The appearance of sharp and strong peaks confirmed the good crystallinity nature of the grown sample.

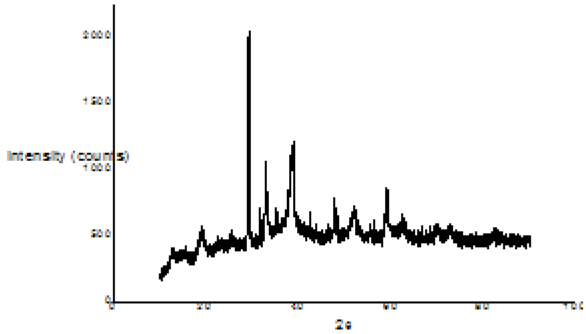


Figure 1: Powder XRD pattern of zinc phthalate crystal

Table 1: Powder XRD data for zinc phthalate crystal

2theta (deg)	*FWHM (deg)*	*FWHM (Radians)*	*Grain Size(nm)*	*Lattice strain*
31.55	0.42	7.326	0.018928	1.83125
19.24	0.85	0.01482	9.3558	0.0037047
25.84	0.47	8.198	0.01708	2.02855
28.09	0.59	0.01029	13.4877	0.00257
37.01	0.25	4.361	0.03179	1.090225
23.57	0.55	9.594	0.01465	2.36495

3.2 FTIR spectrum analysis

The Fourier Transform Infrared Spectroscopy is effectively used to identify the functional groups present in the synthesized compounds. The powdered specimen of zinc phthalate crystal has been subjected to FTIR analysis using KBr pellet technique in the wavelength range between 400 and 4000 $cm^{-1.}$ The observed bands along with their vibrational assignments have been tabulated in the Table 2. The recorded spectrum of zinc phthalate is shown in Fig 2.

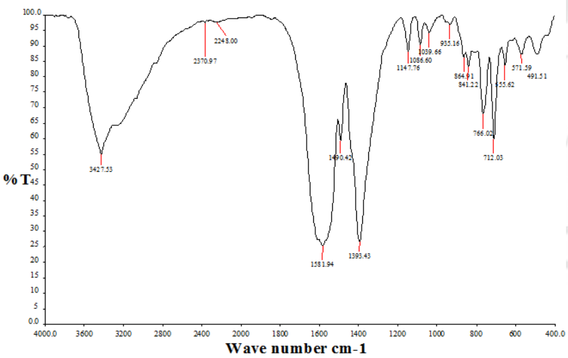


Figure 2: FTIR spectrum of zinc phthalate crystal

Table 2: FTIR data of zinc phthalate crystal

Wave number cm^{-1}	*Assignment*
3427	C-H stretching(Aldehyde)
1490	Aliphatic C=O stretching(ketone)
2370	O-H stretching(Carboxylic Acid)
1147	C-O-C stretching(Ethers)
864	Third overtone C-H stretching
1393	AliphaticC=O stretching(ketone)

3.3 UV-Visible spectrum analysis

Transmission spectra are very important for any NLO material because an NLO material can be used for practical purposes only if it has a wider transparency window. To determine the suitability and transmission range of the zinc phthalate crystal for optical applications, the UV-visible spectrum has been recorded in the range 190-1100 nm by using LAMBDA-35 UV-Vis spectrometer. The recorded spectrum is shown in Fig 3. The lower cutoff wavelength was found to be 292 nm. This π electron dislocation is responsible for its nonlinear optical responses and absorption in near UV region [19]. Thus the grown sample has got a good transmission in UV as well as in visible region 292 -1100 nm and the percentage of transmission is about 52% to 60%. The wide range of transparency of grown sample is an added advantage in the field of optoelectronic application [20] and in the second harmonic generation from the Nd:YAG lasers.

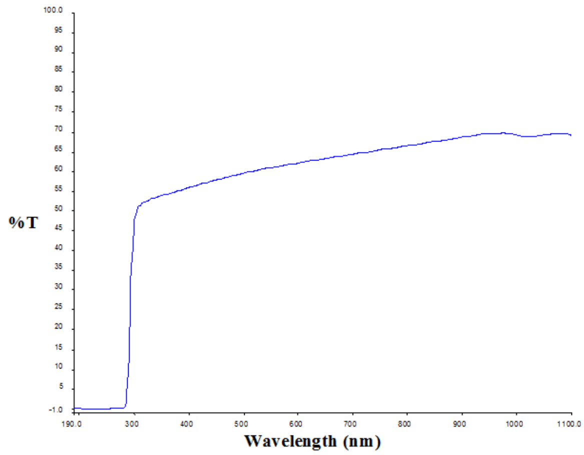


Figure 3: UV-Visible spectrum of Zinc Phthalate crystal

Determination of optical band gap

The dependence of optical absorption coefficient with the photon energy helps to study the band structure and the type of transition of electrons [21]. As a indirect bandgap material, the crystal under study has an absorption coefficient(α) obeying the following relation for high photon energy(hγ)

$$\alpha = \frac{A(h\gamma - Eg)^2}{h\nu}$$

Where E_g is optical band gap of the crystal and A is a material constant. The plot of variation of Photon energy (E) in eV and $(\alpha h\nu)^2$ is shown in Fig 4. The bandgap is found to be 4.21 eV for the grown crystal. As a consequence of wide bandgap, the crystal under study has relatively larger in the visible region [22]. The internal efficiency of the device also depends upon the absorption coefficient. Hence by tailoring the absorption coefficient and tuning the bandgap of the material, one can achieve the desired material which is suitable for fabricating NLO devices as per the requirements.

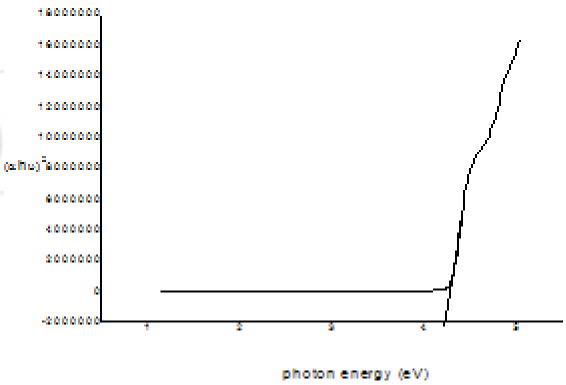


Figure 4: Plot of E Vs $(\alpha h\gamma)^2$ of Zinc Phthalate crystal

3.4 SHG Measurements

The grown crystals have been subjected to SHG studies by Kurtz powder Technique [23] using a fundamental beam of 1064 nm from a Q-switched Nd:YAG laser of pulse energy 1.9 mJ/p with pulse width of 8 ns and repetition rate of 10 Hz, to find out the Non Linear Optical property. The grown crystals are made into fine powder and tightly packed in a micro capillary tube, which serve as the sample cell. SHG output has been confirmed by the emission of green radiation detected by the photo multiplier tube. The results obtained for zinc phthalate shows a powder SHG efficiency of about 1.5 times to that of KDP crystal.

3.5 EDAX Analysis

Energy dispersive X-ray analysis is a technique used to identify the elemental composition of a sample. The observed EDS spectrum of zinc phthalate crystal having the peaks attributed to all the elements at different energies. The recorded spectrum is shown in Fig 5. All the prominent peaks corresponding to different elements in the sample were seen in the spectrum.

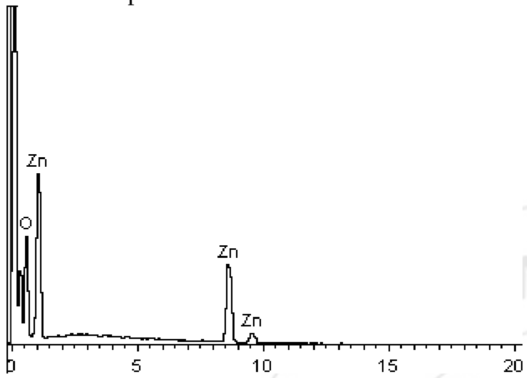


Figure 5: EDAX spectrum of Zinc Phthalate crystal

3.6 Photoluminescence

Photoluminescence (PL) describes the phenomena of light emission from any form of matter after the absorption of photon. PL spectra of zinc phthalate: The unirradiated crystal shows absorption bands attributable to the impurity Zn. To have better understanding of these absorbing species, PL studies were made on exciting the unirradiated crystal with 292nm light, emission bands at 362nm, 399nm and 491nm were observed, Fig 6.

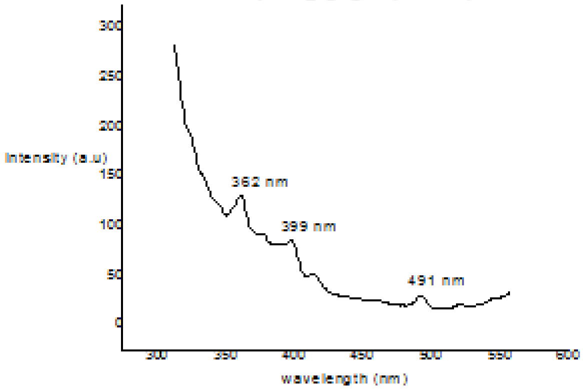


Figure 6: PL spectra of Zinc Phthalate crystal

4. Conclusion

The zinc phthalate crystal has been grown by slow evaporation solution growth technique. Average particle size and lattice strain of the crystals have been determined from the powder X-ray diffraction analysis. Thus we can reduce the size of the crystal in nanometer. The various functional groups present in the crystal have been analyzed by FT-IR spectral studies. The transparency nature of the crystal in the visible and Infrared regions confirms the NLO property of the crystal. The optical behaviour was analyzed using UV-Vis Spectrometer which reveals that the crystal has an extended transparency down to UV and the bandgap estimated for the grown crystal from the optical response curve was found to be 4.21eV. By tailoring the absorption coefficient and tuning the band gap of material we can achieve the desired material suitable for fabricating various layers of optoelectronic devices. The SHG studies for Zinc Phthalate crystal, confirms the enhancement of the NLO property as its efficiency is 1.5 times to that of KDP crystal.

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