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Investigation on the Growth, Optical and Third Order NLO Properties of 2,3-Dimethyl-N-[(E)-2,4,5-Trimethoxybenzylidene] Aniline (DTA) Single Crystal

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Abstract

Good quality third order nonlinear single crystal of 2,3-Dimethyl-N-[(E)-2,4,5-trimethoxybenzylidene] aniline (DTA) was successfully cultivated through the condensation reaction. By following slow evaporation technique, unprecedented single crystal of DTA was grown in the presence of methanol medium. Structural analysis through Single crystal XRD and powder XRD confirms the centric ($P\bar{1}$) space group with triclinic crystal system and the crystallinity of the grown DTA crystal, respectively. Functional group analysis of the title compound was carried out by FTIR studies. Linear optical nature of DTA crystal was ascertained by UV-Vis-NIR and PL analysis. Through UV-Vis-NIR spectrum transmittance efficiency 83% and cut- off wavelength 363nm has been figured out. Emission spectrum from photoluminescence suggests that DTA material can be used as a green light emitting material. Through TG-DSC technique thermal resistance and meting point of DTA crystal was examined. The standard Z-Scan technique was adapted to evaluate the third order nonlinearity of DTA crystal and its third order susceptibility was compared with some of the previously reported NLO crystals. All the above findings indicate that the title DTA crystal can be a smart candidate for NLO application.

1. Introduction

For the few decades many researchers have been working tirelessly in the field of nonlinear optics to find out the most versatile material which possess high NLO property with good stability. But still the quest for that novel material is going on, which makes this field as one of the fascinating fields even today. Nonlinear materials play a significant role in different fields in terms of applications. In particular, they play a vital role in the field of optics such as frequency shifting, optical parametric oscillator (OPO), optical switching, Electro-optic (EO) modulators, frequency mixing, etc. **[1-3]**. Among different classes of NLO materials, organic materials fascinated many researchers due to its flexibility in tailoring the compound based on the required output **[4].** So, many researchers are currently working in exploring new third order nonlinear materials.

Among the used NLO materials, Schiff bases has a special place because of it special feature; relatively large molecular hyperpolarizability which is due to the π- electron delocalization. Currently, in this investigation a Schiff base compound of 2,3-Dimethyl-N-[(E)-2,4,5-trimethoxybenzylidene] aniline (DTA) **[5]** has been synthesized and subjected to various characterizations to figure out its crystalline nature, linear optical nature and third order nonlinear properties, which has been reported for the first time. Extensive literature survey also confirms that, so far, no outcomes were available on the physio – chemical properties of the title DTA crystal.

2. Synthesis

The condensation reaction between the 2,3,5-Trimethoxy benzaldehyde and 2,3 Dimethyl aniline leads to the formation of a Schiff base compound 2,3-Dimethyl-N-[(E)-2,4,5-trimethoxybenzylidene] aniline (DTA) with imine (C=N) functional group and water; which is a byproduct. Equal ratios (1:1) of reagents were taken in a round bottom flask (RBF) with 25 ml methanol solution. This mixture was refluxed for 45 min at 40° C, which results in the formation of a violet solution. The obtained solution was allowed to cool down at room temperature, after 48 hours, yellow precipitates were obtained. The obtained yellow precipitate was dissolved in a mixed solvent of methanol and acetone. This resulting mixture was placed in a magnetic stirrer till a homogenous solution was obtained. With the help of aluminum foil which has few minute pores on it, the homogenous solution is lidded and placed under room temperature to undergo slow evaporation.

3. Results and Discussions

Powder X-Ray Diffraction

PXRD studies were carried out with fine powders, which has been grinded from high quality DTA single crystal. High sharpness and high intensity of the prominent peak at particular 2θ angle confirms the high crystalline nature, phase purity and formation of the title compound. Experimental acquired powder XRD pattern of the title crystal is presented in Fig. 1. Also, the peaks clearly indicate the absence of solvent consolidation.

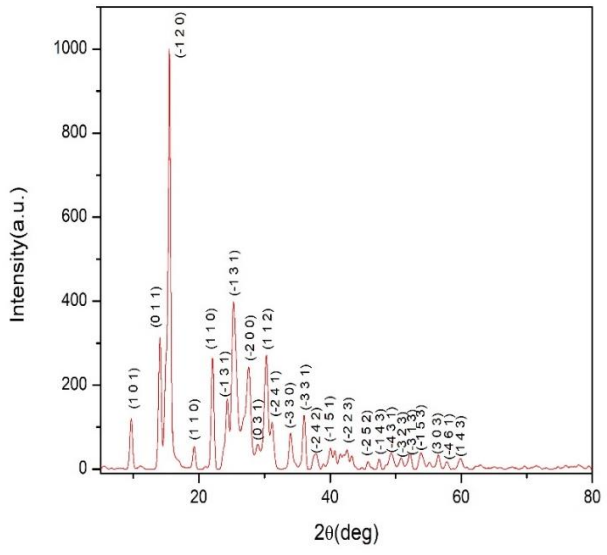

Fig.1 Obtained Powder XRD pattern of DTA

Optical transmission spectrum of DTA single crystal

From NLO point of view, two major factors which determine the role of crystals in terms of application are lower cut-off wavelength and transmittance percentage. In order to elucidate it, 1.8 mm thickness DTA crystal is subjected to UV-Vis-NIR studies. Fig 2 depicts the obtained UV graph. From the graph the λ_{max} is found out to be 363 nm, which is in the π-π^* regime. Transmittance efficiency of DTA crystal is 83%, no more extra peaks was visible beyond λ_{max} which signifies that DTA can also be used in optical field.

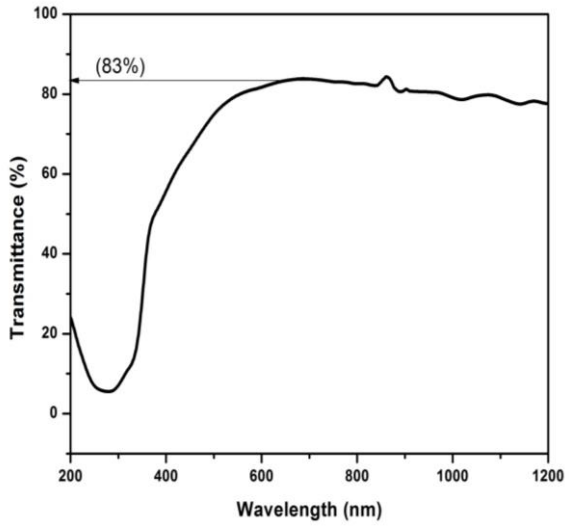

Fig. 2 Optical transmittance of DTA

Photoluminescence Study

The luminescence property of the DTA crystal was explored by using Photoluminescence study, as it is non-destructive and reliable. This maximum absorption is the excitation wavelength, which was fixed from the UV analysis. With 406 nm as excitation wavelength, the PL spectrum of DTA crystal was recorded and the same is shown in the fig 3. From the graph it is obvious that the emission peak is at 535 nm, which falls in the green region. The maximum intensity occurred in 535 nm that it belongs to $\pi - \pi^*$ transition, which was attributed by the highly conjugated (C=N) double bond. The obtained result portraits that the grown DTA crystal can be used as new material for the emission of green light.

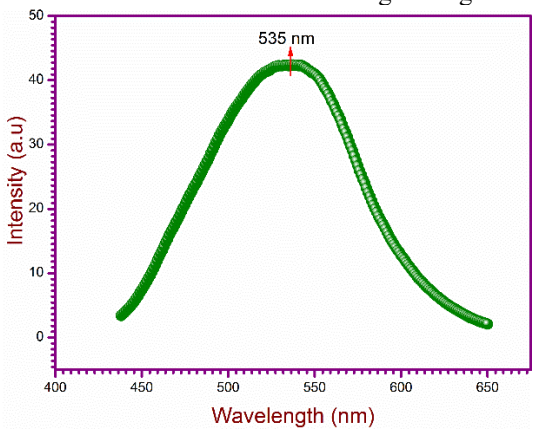

Fig. 3 PL graph of DTA crystal

Z-Scan measurement

Z-scan technique which is one of the common methods adapted to investigate the third order nonlinear properties. Through this experiment two fundamental parameters namely Nonlinear Refractive Index (NLRI) and Nonlinear Absorption (NLA) was obtained, third order susceptibility determines how effectively this crystal can be used in NLO application. He-Ne laser with emission wavelength of 632.8 nm was used as source. Conversion of laser beam into Gaussian beam was done with the help of Gaussian filter. The main advantage of Gaussian beam is, both the intensity and electric field is uniformly distributed throughout the beam. In Z-scan technique two methods has been incorporated namely open aperture (OA) and closed aperture (CA) to calculate nonlinear absorption co-efficient (β) and nonlinear refractive index (n_2) respectively.

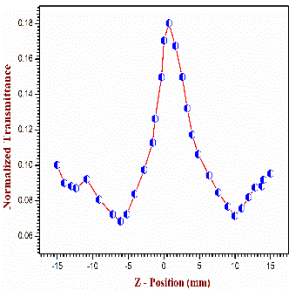

Fig. 4 Normalized transmittance in the open aperture condition

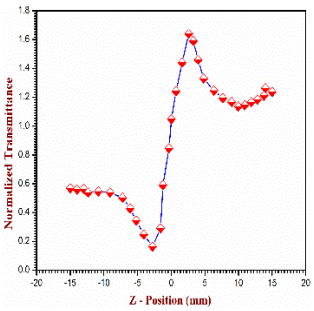

Fig. 5 Closed aperture (CA) Z-scan profile of DTA crystal.

Table I Non-linear parameters obtained from Z-scan technique

Parameters	Obtained Values
Nonlinear refractive index (n_2)	4.511 x 10^{-5} m/W
Nonlinear absorption co-efficient (β)	3.480 x 10^{-11} m^2/W
Third-order nonlinear optical susceptibility ($\chi^{(3)}$)	7.012 x 10^{-5} esu

4. Conclusion

An organic single crystal of 2,3-Dimethyl-N-[(E)-2,4,5-trimethoxybenzylidene] aniline (DTA) was successfully grown at room temperature through slow evaporation process. Unit cell parameters and the centrosymmetric nature ($P\bar{1}$) of the grown crystal were confirmed by single crystal X-ray diffraction. Transparency region 83%, lower cut off wavelength 363nm of DTA crystal was obtained from the spectrum of UV-Vis-NIR analysis. With these characterization results as a support, we can conclude that the grown DTA crystal is a suitable compound for nonlinear applications.

References

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