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# Growth, Structural, Spectral and Nonlinear Optical investigations of 2,4-Dinitrochlorobenzene (DNCB) Crystals

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**ABSTRACT:** The title crystal was grown from ethanol solvent by slow evaporation method. In order to good quality of crystals involved various analytical techniques. The crystal structure was verified by single crystal X-ray diffraction (SXRD) and structural purity was revealed by powder X-ray diffraction (PXRD). The functional group of the grown crystal was examined by FTIR spectrum. From the UV-Visible spectrum, grown crystal found that there is no absorption in the entire visible region. Thermal stability of the grown crystal was identified by TGA-DTA and DSC studies. The physical stability of the grown crystal was measured by Vicker's microhardness studies. The Nonlinear optical eccentric was evaluated by Kurtz-Perry powder technique.

**KEYWORDS:** Slow evaporation, Ethanol, Single-XRD, Micro hardness, Second Harmonic Generation.

## 1 INTRODUCTION

This short assessment presents an account of the research on organic nonlinear optical (NLO) crystalline materials with second order nonlinear efficiency. Organic crystals are usually assembled from discrete units of organic molecules and also organic molecular crystals must possess suitable electronic and structural properties. Hence most of the organic compounds are crystallized and studied due to their nonlinear optical (NLO) effects [1]. If the electronic structure of the molecular unit and the geometric crystalline structure of a given organic crystal are known, all of its NLO properties can be calculated. Theoretically this stage is explained by a very simple two level model on the basis of which it is relatively easy to predict and estimate the value of the hyperpolarizabilty β of a molecule ([2],[3],[4]). Currently organic crystals played an important role as NLO materials. Compared to their inorganic counterparts, organic NLO materials have advantages such as large NLO coefficients and structural diversity or flexibility and higher order hyper polarizabilty and higher order of optical transparency [5].The nonlinear effects, including strong donor-acceptor intermolecular interactions and delocalized pi-electron systems, are reasonably well understood [6]. A halogen with dinitro substituted derivatives of aromatic ring used as optical nonlinear promising materials for future optoelectronic and nonlinear optical applications [7]. 2,4-dinitrochlorobenzene is a chlorine and two nitro groups substituted aromatic compound with following characteristic: melting point 54˚C, molecular weight 202.55 and molecular formula $C_6H_3ClN_2O_4$, its molecular structure is shown in figure 1. Even though 2,4-dinitrochlorobenzene is called 1-chloro-2,4-dinitrobenzene, it has been used in industry such as synthesis drug and chemical reagent and many other purpose ([8], [9],[10])**.** In this paper, we discussed growth and the studies of crystal structure, vibrational, optical, mechanical properties of 2,4-dinitrochlorobenze (DNCB) crystals.

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## 2 EXPERIMENTAL

To grow bulk crystals from solution by slow evaporation method, it is desirable to select a solvent in which it is moderately soluble. The size of the crystal mainly depends on the amount of material available in the solution. 2,4-dinitrochlorobenzene is insoluble in water. But it is moderately soluble in concentrated ethanol. Hence we have attempted to grow bulk crystals of DNCB using ethanol as solvent. The commercially available 2,4-dinitrochlorobenzene (97% pure chemical purchased from Sigma-Aldrich) was purified by repeated recrystallization process using ethanol and the recrystallized salt was taken as the raw material for growth. The solvent was taken in a beaker and purified material was added gradually and stirred continuously until to attain supersaturated solution.

The supersaturated solution was filtered using a glass filter paper of 1µm porosity. The filtered solution was tightly closed with thick filter paper so that the rate of evaporation could be minimized. Good optical quality crystals of dimension were obtained after 2 weeks. The grown crystal is shown in figure 2.

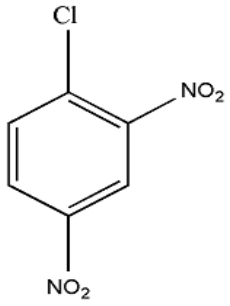


*Fig. 1. Molecular structure of DNCB*

*Fig. 2. As grown crystal of DNCB*

### 2.1 CHARACTERIZATION STUDIES

The grown crystal has been analyzed by different instrumentation methods in order to check its suitability for device production. Single crystal X-ray diffraction analysis and Powder X-ray diffraction analysis has been carried out for the grown crystal of DNCB. The existence of functional groups has been identified from the Fourier transform infra-red (FT-IR) spectral analysis. Its optical quality has been analyzed by UV-Visible spectral analysis. Thermal stability has been analyzed by Thermogravimetric –Differential thermal analyzer (TGA-DTA) and Differential Scanning calorimetric (DSC) analyzer. Mechanical stability of the crystal has been measured by Vicker's microhardness test. The relative second harmonic generation has been carried out by Kurtz-Perry powder technique in order to confirm its second harmonic generation efficiency.

## 3 RESULTS AND DISCUSSIONS

### 3.1 SINGLE X-RAY DIFFRACTION STUDIES

The unit cell dimensions of grown DNCB crystal was analyzed from single crystal X-ray diffraction studies by using Bruker axs kappa apex2 CCD diffractometer with the source of fine focused sealed tube , graphite monochromator and MoKα (λ= 0.71073 Å) radiation. From the X-ray analysis, we found that the grown crystal belongs to orthorhombic system with space group of Pccn. The cell parameters are $a$ = 8.9291 Å, $b$ = 11.0347 Å, $c$ = 15.6707 Å and $\alpha$ = 90˚, $\beta$ = 90˚, $\gamma$ = 90˚ and volume of

the unit cell is $V$ = 1554.03 Å$^3$. The crystallographic data of the crystal are well coincide with the literature ([11], [12]).The comparative structural data for DNCB is presented in table 1. The ORTEP graphical diagram is shown in figure 3.

***Table 1. Comparative structural data for DNCB***

| Lattice parameters | Wilkins et al(Å) | Sethuraman et al(Å) | Present Value(Å) |
|---|---|---|---|
| a | 8.93 | 8.9355 | 8.9291 |
| b | 11.03 | 11.0586 | 11.0347 |
| c | 15.84 | 15.7053 | 15.6707 |

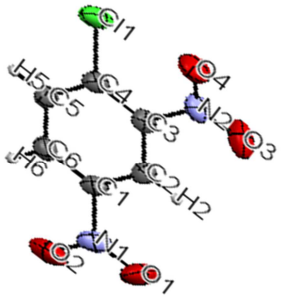


***Fig. 3. ORTEP diagram of DNCB crystal***

### 3.2 POWDER X-RAY DIFFRACTION STUDIES

The grown DNCB crystal was characterized by powder X-ray diffraction using Rigaku mini Flex II X-ray diffractometer with CuKα (1.54059Å) radiation at ambient temperature. When X-ray falls over a crystalline powder, it diffracts in a pattern characteristic to form its structure. Hence, the diffraction pattern is obtained from a powder of the material, quite than an individual crystal. A diffraction pattern plots scattered intensity against the angle of the detector, 2θ. The sharp and very intense XRD peaks were indexed and their confirmed that the material has the crystalline character [13]. The powder diffraction spectrum for DNCB crystal is shown in figure.4

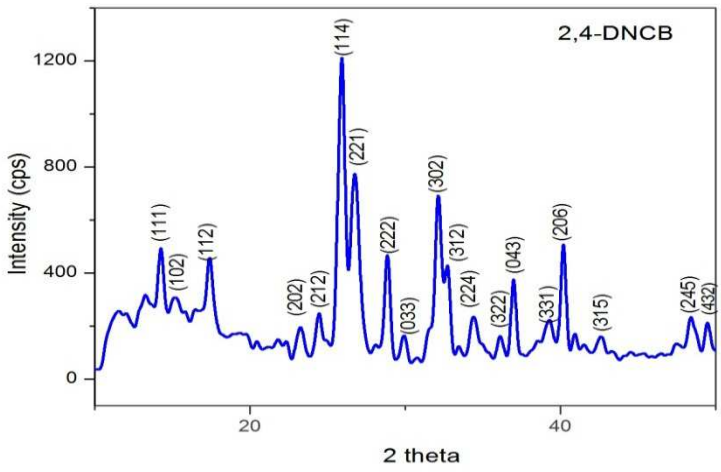


***Fig. 4. Powder XRD spectrum of DNCB crystal***

### 3.3 FT-IR CHARACTERIZATION

The FTIR analysis of DNCB was carried out to confirm the existence of functional groups and their vibrational modes. The Fourier transform infrared spectrum of DNCB was recorded in the region 400– 4000 $cm^{-1}$ (± 4 $cm^{-1}$) with Perkin Elmer Fourier transform infrared spectrophotometer (model SPECTRUM RX1) using KBr pellets containing DNCB powder obtained from the grown single crystals. The observed FTIR spectrum is shown in figure 5. The vibrational assignment of the DNCB crystal is noted in table 2. In the higher energy region, there is a peak at 3396.51 $cm^{-1}$ due to C–H stretch of the aromatic ring. The low intensity absorption is observed in the frequency 2361.83$cm^{-1}$ due to C–N stretching. The peak at 1639.86 $cm^{-1}$ is common to C–C stretching vibrations. The sharp peak was positioned at 1408.19 $cm^{-1}$ assigned to symmetric vibrations of the nitro groups. The sharp peak was positioned at 598.11$cm^{-1}$ due to halogen substituted in benzene derivative that is, C–Cl stretching vibration [14].

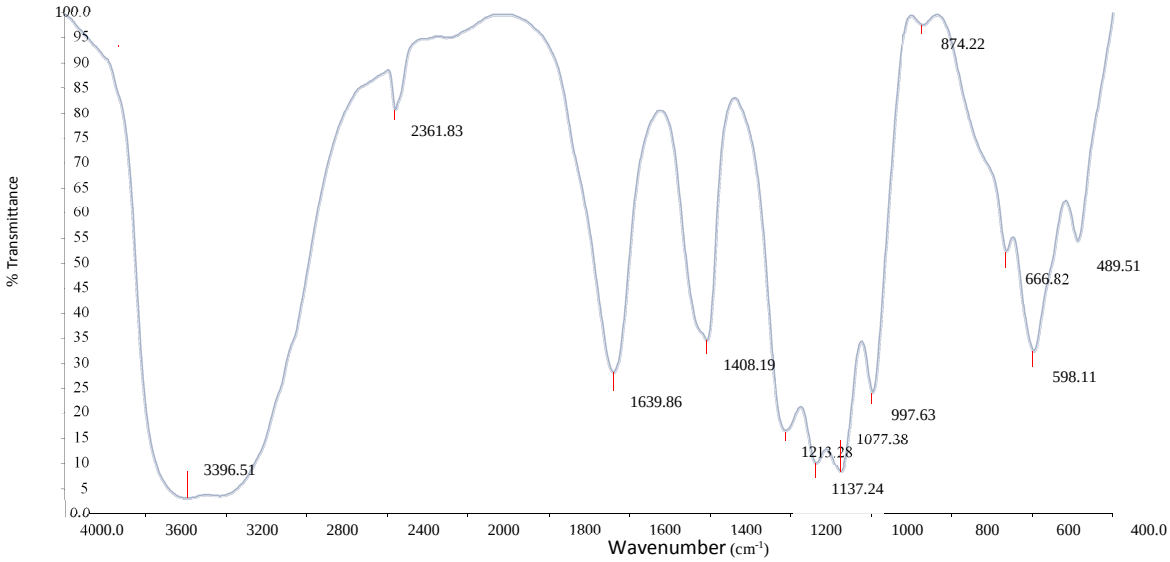


***Fig. 5. FTIR Spectrum of DNCB crystal***

***Table 2. FT-IR Vibrational band assignments of DNCB crystal***

| Wave number ($cm^{-1}$) | Vibration Assignments |
|---|---|
| 598.11 | C–Cl stretching |
| 874.22 | Asymmetric ring stretching |
| 1077.38 | C–N in plane bending |
| 1408.19 | Symmetric mode of the $NO_2$ groups |
| 1639.86 | C–C stretching in ring |
| 2361.83 | C–N stretching |
| 3396.51 | Aromatic CH stretching |

### 3.4 UV-VISIBLE CHARACTERIZATION

The optical transmittance of DNCB crystals was recorded in the region 190–1100nm using LAMBDA-35 UV–Vis spectrophotometer, which includes near UV, visible and far IR regions. The UV-Vis transmittance spectra of the grown DNCB crystal is shown in figure 6. The cutoff wavelength of the DNCB crystal is around 310 nm. From the cut off wavelength entirely no absorption in the visible region. In the entire visible region, the transmittance is greater and the absorption is very less and for the incident light wavelength 310–1100 nm. This nature in the visible region is required for nonlinear optical applications [15].

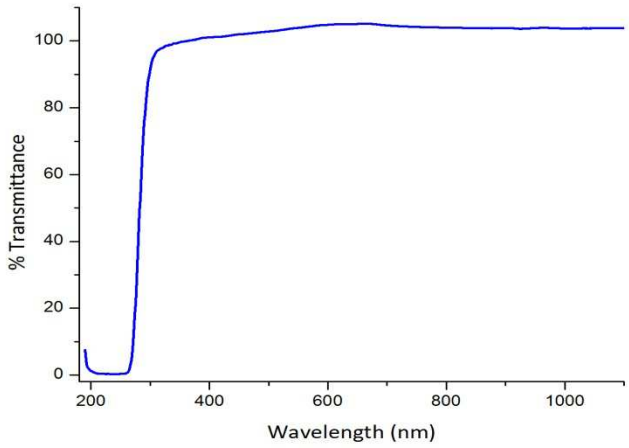


*Fig.6. UV-Vis. transmittance spectrum of DNCB crystal*

### 3.5 THERMAL STUDIES

Thermogravimetric and differential thermal analysis (TGA-DTA) of DNCB crystal were carried out by simultaneously in $N_2$ gas atmosphere at a heating rate of 10˚C / minute for a temperature range of 30˚C– 400˚C using NETZSCH - STA 449 F3 JUPITER simultaneous thermal analyzer system. The recorded curves of TGA-DSC are shown in figure 7. It is evidently observed from the TGA spectrum that material has good thermal toughness up to 182˚C. The major weight loss (99%) of sample occurred from the temperature range 182˚C to 312˚C. One important observation is that, there is no phase transition till the material melts and this improves the temperature range for the utility of the crystal for NLO applications. In the DTA curve, Two endothermic peaks were observed at 54˚C and 312˚C. The first endothermic peak at 54 ˚C represents the melting point of the DNCB crystal and the second endothermic peak at 312 ◦C represents around its boiling point. After melting, no specific exothermic or endothermic peaks were observed up to 312˚C which shows that there is no degradation of the crystal above the melting point up to 312˚C. The sharpness of the endothermic peaks observed in DTA indicates good degree of crystallinity of the sample [16].

The Differential Scanning Calorimetric analysis was also carried out for sample of DNCB crystal by using same NETZSCH - STA 449 F3 JUPITER simultaneous thermal analyzer system. A detailed inspection of DSC curve is shown in figure 8. From the DSC curve, there are two major changes takes place while heating the sample, first endothermic peak at 58°C, second at 312°C temperature respectively. The first and second endothermic peaks correspond to melting point and boiling point of the sample. The exothermic dip point at 324°C corresponds to the decomposition of DNCB crystal into various gaseous products like $NO_2$, NO etc [17].

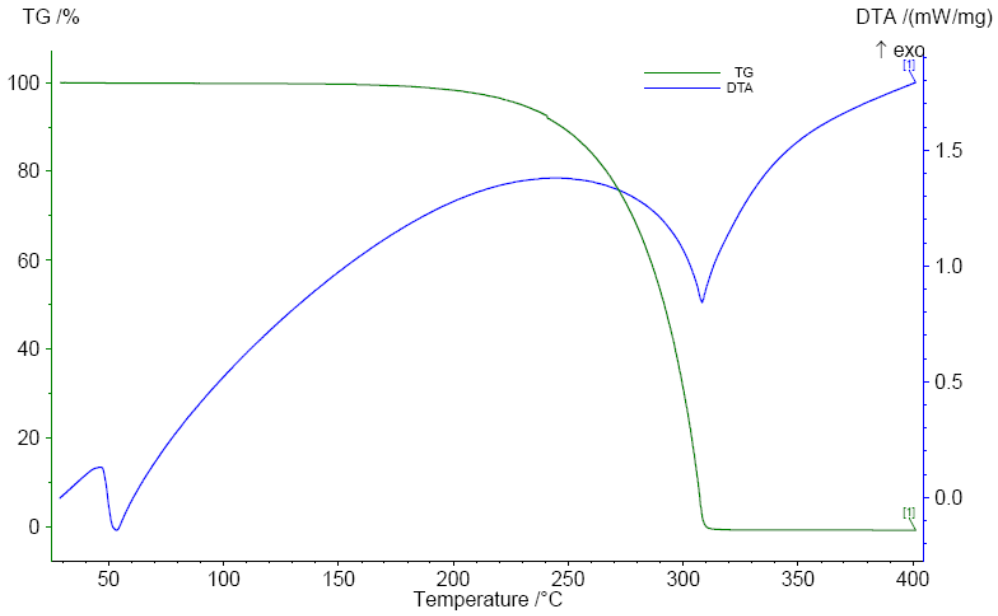


*Fig.7. TGA-DTA curve of DNCB crystal*

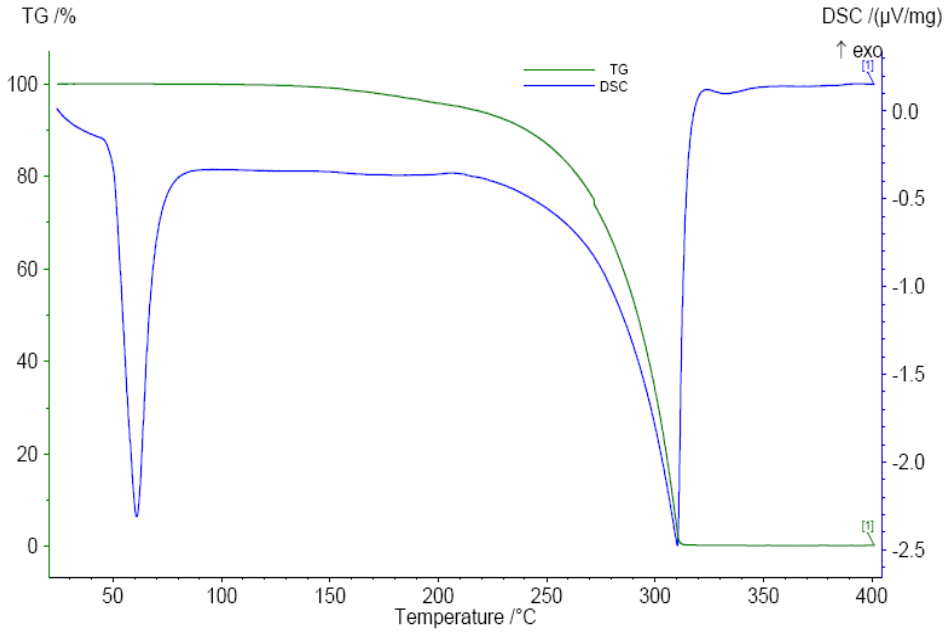


*Fig.8. DSC curve of DNCB crystal*

### 3.6 MECHANICAL STUDIES

The physical stability of DNCB crystals were carried out using SHIMADZU (HMV-2T) Vicker's micro hardness tester fitted with a diamond indenter. The measurement was done at different points on the crystal surface and the average value was taken as the Hv for a given load.

The micro hardness was calculated using the relation

$$H_v = 1.8544\ P/d^2\ (kg/mm^2)$$

Where P is the applied load and d is the diagonal length of the indentation impression.

The calculated Vicker's hardness values for DNCB crystals as a function of load is shown in figure 9. The normal indentation size effect (ISE) involves decrease in hardness value with increasing load and the reverse indentation size effect (RISE) involves increase in hardness values with increasing load. There are many examples of normal occurrence of ISE in brittle materials and RISE occurs in single crystals, which undergo plastic deformation ([18],[19],[20])**.** As grown DNCB crystals exhibit RISE, since indenter infiltrates only the surface layers at lower loads. By plotting (Figure 10) log P *vs* log d, the value of work hardening coefficient n is calculated as 3.888, which confirms that the crystal belongs to the category of soft materials ([21],[22]).

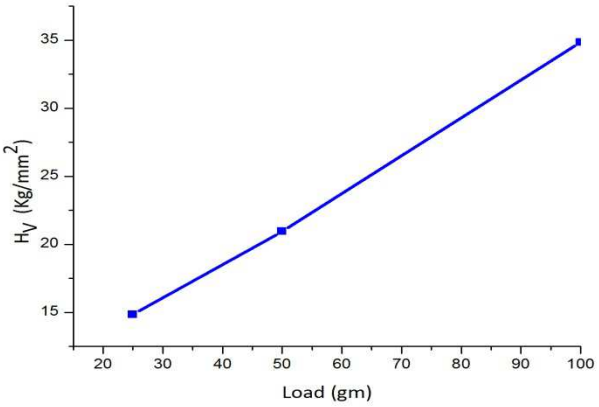


***Fig .9. Hardness number versus load***

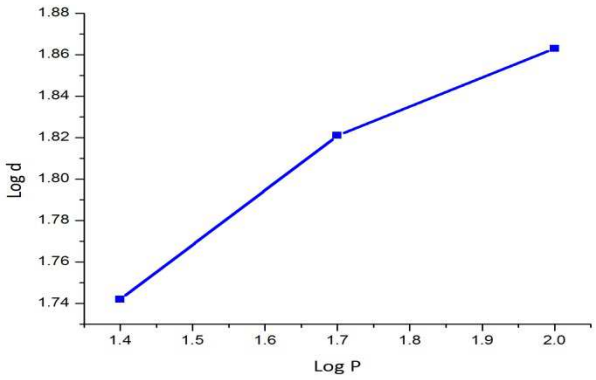


***Fig .10. Log P versus Log d***

### 3.7 NLO CHARACTERIZATION

The powder crystals of DNCB employed into Kurtz-Perry powder technique [23]. The finely powdered sample of DNCB crystal was densely packed in very in thin glass tube. A Nd-YAG laser beam of 1064 nm wavelength (8ns pulse width with 10Hz pulse rate was made to fall normally on the sample, the second harmonic generation is estabilished by emission of green radiation from sample. Second harmonic generation (SHG) is a very powerful technique for checking nonlinear optical behavior of a crystal. Generally non- centro symmetric crystals exhibits second harmonic generation but sometimes any break of centro symmetry will lead to the second harmonic generation. Even though the crystal of DNCB belongs to centro symmetric, it exhibits SHG activity due to charge transfer interactions between donor and acceptor [24]. KDP crystals were powdered to the identical size and were used as reference materials in the SHG measurement. The relative SHG efficiency of DNCB was found to be half the times that of KDP and 1.3 times lesser than that of Urea.

## 4 CONCLUSION

Single crystal of DNCB was grown by the slow evaporation method from ethanol solution. From the result of FTIR, functional group characteristic frequencies of DNCB crystals was revealed. Single XRD studies stated that DNCB crystals belongs to orthorhombic system with space group pccn. Crystalline perfection was explained by the Powder XRD results. The optical, thermal and mechanical studies indicate that DNCB was a potential material for electro-optical industry.

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## REFERENCES

[1] Min-hua Jiang and Qi Fang, "Organic and Semi organic Nonlinear Optical Materials," *Advanced Materials*, vol.11, no. 13, pp. 1147–1151, 1999.

[2] J. L. Oudar and D. S. Chemla, "Hyperpolarizabilities of the nitroanilines and their relations to the excited state dipole moment," *The Journal Chemical Physics*, vol.66, pp. 2664-2668, 1977.

[3] W. H. Thompson, M. Blanchard-Desce, V. Alain, J. Muller, A. Fort, M. Barzoukas and J. T. Hynes, "Two valence bond state model for molecular nonlinear optical properties. Comparison with push-pull polyene solution measurements," *Journal of Physical Chemistry A*, vol.103, pp.3766-3771, 1999.

[4] Henryk Ratajczak, Jan Baran Austin J.Barnes, Jőzef Barycki, Solange Debrus, Zdzislaw Latajka, Marie May, Adam Pietraszko , "Structural and vibrational study of a novel nonlinear optical material: 3-nitrobenzoic acid hydrazide", *Journal of Molecular Structure*, vol.596, no.1, pp. 17-23, 2001.

[5] David P. Shoemaker, Jerry Donohuem, Verner Schomaker and Robert B. Corey, "The Crystal Structure of Ls-Threonine," *Journal of the American Chemical Society,* vol. 72, no.6, pp. 2328-2349, 1950.

[6] G. R. Snyder, A.U. Chowdhury, and G. J. Simpson "Exciton Coupling Model for the Emergence of Second Harmonic Generation from Assemblies of Centro symmetric Molecules," *Journal of Physical Chemistry A,* vol.118, no.24, pp.4301-4308, 2014.

[7] A.Stanculescu and F.Stanculescu, "Some optical investigations on crystalline doped meta-dinitrobenzene", *Journal of optoelectronics and advanced materials, v*ol.2. no.5, pp.536-541, 2000.

[8] N. Muniyandi, S. Vasudevan and S. Pitchumani, "Performance characteristics of chloro-substituted dinitrobenzene for magnesium reserve batteries", *Journal of Power Sources*, vol. 45, pp.119–130, 1993.

[9] R. Kalaivani, R.Malarvizhi and R. Subbalakshmi, "Synthesis of a novel barbiturate from 1-chloro-2,4-dinitrobenzene as an anticonvulsant agent," *Medicinal Chemistry Research* , vol.17, pp.369–373, 2008.

[10] Ayhan Usta, Mehmet Zengin and Mehmet Birey, "Identification of radical structure in 2,4-dinitrochlorobenzene single crystal by EPR," *Romanian Journal of Physics***,** vol. 56, no. 9–10, pp.1162–1166, 2011. (Bucharest)

[11] A. Wilkinks, R.W.H. Small and J.T. Gleghorn, "Polymorphism of 1-chloro-2,4-dinitrobenzene: structures of α and β forms," *Acta Crystallographica Section B,* vol. B46, pp.823–826, 1990.

[12] K. Sethuraman , R. Ramesh Babu , N. Vijayan , R. Gopalakrishnan and P. Ramasamy, "Growth and characterization of organic nonlinear optical crystal of 1-chloro-2,4-dinitrobenzene (CDNB)," *Spectrochimica Acta Part A*, vol.66, pp.707-711, 2007.

[13] M.R.Jagadeesh, H.M.Suresh Kumar and R. Ananda Kumari,"Growth and characterization of an organic NLO crystal: L-alanine-2-furoic acid," *Archives of Applied Science Research*, vol.6, no.4, pp.188-197, 2014.

[14] R.M. Silverstein and F.X. Webster, *Spectrometric Identification of Organic Compounds*, sixth Ed. John Wiley Eastern & Sons Inc., Canada, 1998.

[15] S.Natarajan, S.A. Martin Britto and E. Ramachandran, "Growth, Thermal, Spectroscopic, and Optical Studies of L-Alaninium Maleate, a New Organic Nonlinear Optical Material,"*Crystal Growth & Design,* vol. 6, no.1, pp.137-140, 2006.

[16] M. Lenin and P. Ramasamy, "Synthesis, growth and characterization of 3-nitroacetanilide—A new organic nonlinear optical crystal by Bridgman technique," *Journal of Crystal Growth,* vol.310, pp.4451– 4455, 2008.

[17] M. N. Rode, G. G. Muley, D. V. Meshram, S. S. Hussaini, V. G. Dongre, B. H. Pawar and M. D. Shirsat, "Growth and characterization of L-tartaric acid doped and mixed Di-sodium hydrogen phosphate (DSHP) single crystal for laser applications," *Optoelectronics and advanced materials – Rapid communications*, vol. 3, no. 9, pp. 927 – 932, 2009.

[18] J. Gong and Y. Li, "An energy-balance analysis for the size effect in low-load hardness testing," *Journal of Materials Science*, vol.35, no.1, pp-209-213, 2000.

[19] H. Li, Y. H. Han and R. C. Bradt, "Knoop microhardness of single crystal sulphur," *Journal of Materials Science,* vol.29, no.21, pp.5641-5645, 1994.

[20] T. Kanagasekaran, P. Mythili, P. Srinivasan, N. Vijayan, G. Bhagavannarayana, P. K. Kulriya, D. Kanjilal, R. Gopalakrishnan and P. Ramasamy, " Effects of 50 MeV Si ion irradiation on nonlinear optical benzimidazole single crystals," *Crystal Research and Technology*, vol.42, no.12, pp.1376-1381, 2007.

[21] E.M .Onitsch, "Über die Mikrohärte der Metalle," *Mikroskopie*, vol. 2, pp.131-151, 1947.

[22] C.Besky Job, J.Benet Charles, "Growth, structural and microhardness studies of $KSb_2F_7$ and $KSb_4F_{13}$ crystals," *Indian Journal of Pure & Applied physics,* vol. 49, pp.820-824, 2011.

[23] S.K.Kurtz and T.T.Perry, "A Powder Technique for the Evaluation of Nonlinear Optical Materials," *Journal of Applied Physics*, vol. 39, no.8, pp.3798-3813, 1968.

[24] Jerry I. Dadap, Jie Shan and Tony F. Heinz, "Theory of optical second-harmonic generation from a sphere of centrosymmetric material: small-particle limit," *Journal of Optical Society of America B*, vol. 21, no. 7, pp.1328-1347, 2004.