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Investigations on the growth and characterization of NLO active Cadmium Picrate single crystal

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Abstract - *Single crystal of Cadmium Picrate has been grown from aqueous solution by slow evaporation solution growth technique. The lattice dimensions have been identified from single crystal and powder X-Ray diffraction measurements. The vibrational frequencies of various functional groups in the crystals have been confirmed by the FT-IR spectrum. Transmission range of the crystal has been determined by UV-Vis-NIR spectra. The mechanical stability of the grown crystal has been derived from Vickers micro hardness study. The dielectric response has been studied for different frequency ranges by parallel plate capacitor technique. The enhancement in the NLO property of the grown crystals using KDP crystal as a reference has been studied using SHG measurements.*

***Key Words*: X-ray diffraction;. Growth from solutions; Nonlinear optical materials; Dielectric materials.**

1. INTRODUCTION

The most efficient nonlinear optical (NLO) frequency conversion materials are the important requirement for many applications in the field of Photonics and optoelectronics [1–3]. More recent works have demonstrated that organic crystals will have very large nonlinear susceptibilities compared with that of inorganic crystals, but their uses are impeded by poor mechanical properties and the inability to produce large crystals. Purely inorganic NLO materials typically have excellent mechanical and thermal properties with relatively modest optical nonlinearities [4]. In view of this, a new approach has been developed to combine the favorable aspects of both organic and inorganic molecules to form semi-organic compounds. In semi-organics, polarizable organic molecules are stoichiometrically bound within an inorganic host [5]. Picric acid (2,4,6-trinitrophenol) is an organic acid, which is used in the dyeing industry and as an explosive. The presence of three electrons withdrawing Nitro groups make it as a good acceptor for neutral carrier donor molecule [6-8]. The metal derivatives of picric acid are helpful in homeopathic medicine and it shows the extraordinary variety in the bonding of metal salts and complexes [9]. The explosive characteristics of the metallic salts of picric acid are of interest in the technology of explosives chiefly because of the ease with which picric acid combines with many metals and basic compounds to form picrates, some of which are capable of direct detonation when subjected to heat or shock. Picric acid [10] and its complexes with amino acids, viz., l-prolinium picrate, l-valinium picrate and l-asparaginium picrate and Glycine picrate show very high second harmonic generation efficiency [11-14]. Motivated by these considerations an attempt has been made to grow an another material such as cadmium Picrate single crystals.

2. EXPERIMENTAL PROCEDURE:

MATERIAL SYNTHESIS AND CRYSTAL GROWTH

The saturated cadmium picrate solution was prepared by dissolving analar grade Picric acid ($C_6H_3N_3O_7$), and Cadmium Acetate ($C_4H_6CdO_4 2H_2O$) in Acetone. The saturated solution was stirred in a magnetic stirrer for 5 hours, to get homogenous mixture. The synthesized salt was taken and the saturated solution was prepared in accordance with the solubility data. Slow evaporation of the solvent at room temperature yielded many small crystals. The solution was then covered with a perforated polythene paper. The beaker containing the solution was kept in an undisturbed environment for slow evaporation. Transparent yellow colour Cadmium Picrate crystals were harvested in a growth period of 14 days as shown in Fig - 1. Best crystals were selected from the parent solution and it was used for characterization analysis.

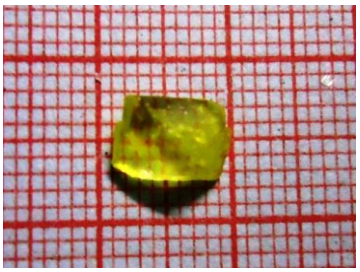

Fig - 1: As grown Cadmium picrate crystal

3. CHARACTERIZATION STUDIES, RESULTS AND DISCUSSION

3.1. SINGLE CRYSTAL X-RAY DIFFRACTION ANALYSIS

The grown crystal has been subjected to single crystal X-ray diffraction studies using Enrafnonius CAD4 X-ray diffractometer to determine the unit cell parameters. The obtained lattice parameter values of the crystals are tabulated in Table-1

Table–1: Single crystal XRD data for Cadmium Picrate crystal

Cell Parameters	a = 6.7680 A°
	b = 9.2758 A°
	c = 13.6137 A°
	$\alpha = \gamma = 90°$
	$\beta = 104.15°$
Volume	828.65 A^3
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3.2. POWDER X- RAY DIFFRACTION ANALYSIS

The grown sample which has been subjected to Powder X-Ray diffraction using DIMAX ULTIMA-III with (λ=1.5406A^o) radiation. The observed powder XRD pattern of Cadmium Picrate crystal is shown in Fig.2. The well-defined peaks at specific values show high crystallinity of the grown crystals. From the observed pattern, the average grain size and lattice strain of the Cadmium Picrate crystal are calculated using the Scherrer formula, D=0.9 λ /β cosθ where λ is the wave length of copper k $_\alpha$ line (1.54056 A^o), θ is the diffraction angle, β is the full width half maximum of the peak and D is the average particle size. It concludes that the grown Cadmium Picrate crystal is 24.959 micrometers in size, and the lattice strain is found to be 0.00030511.

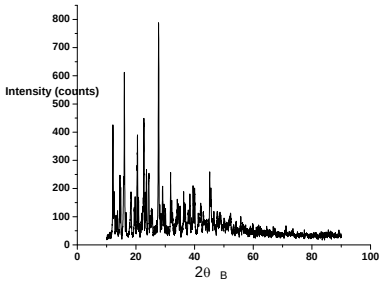

Fig-2: Powder XRD pattern of Cadmium Picrate crystal

3.3 EDAX ANALYSIS

Energy dispersive X-ray analysis is a technique used to identify the elemental composition of a sample. The observed EDS spectrum of Cadmium Picrate crystal having the peaks attributed to all the elements at different energies is depicted in Fig.3 which confirms the presence of elements in the crystal. All the prominent peaks corresponding to different elements in the sample can be seen in the spectrum.

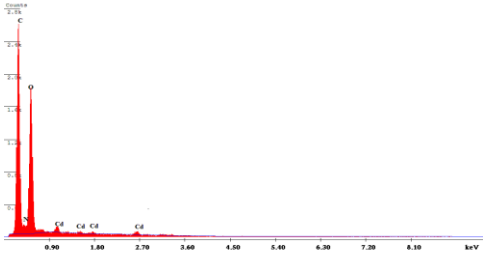

Fig-3: EDAX spectrum of Cadmium Picrate crystal

3.4 FTIR SPECTRUM ANALYSIS

The Fourier Transform Infrared (FTIR) Spectrum has been recorded for the sample in the range of 400-4000 cm^{-1} following the KBr pellet technique employing Braker, IFS 66 FTIR spectrometer and it is shown in Fig.4. The tentative assignments for the absorption bands in the spectrum are given using the available IR spectral data and the corresponding vibrational group assignments are given in the Table 2 which shows the confirmation of the grown crystal.

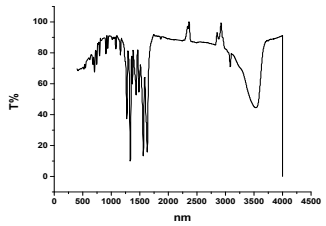

Fig - 4: FTIR Spectrum of Cadmium Picrate crystal

Table -2: FTIR data of Cadmium Picrate crystal

Wave Number in Cm^{-1}	Assignment
804	C-O stretch
920	O-H bend (Carboxylic acid)
1086	C-O stretch, C-N stretch
1155	Phenolic O vibration
1163	C-O stretch
1330	NO_2 symmetric stretch
1484	N-O asymmetric stretch

3.5 UV-VIS SPECTRUM ANALYSIS

The transmission range and transparency cutoff wavelength are very important parameters, especially for crystals used in SHG. The optical transparencies of cadmium picrate crystals has been analyzed by subjecting the specimen to UV-Vis-NIR spectral analysis using LAMBDA-35 UV-visible spectrophotometer within the wavelength range of 190 nm to 1100 nm and the observed spectra of Cadmium Picrate crystal is shown in Fig.5. The lower cutoff wavelength of the grown crystal is found to be 310 nm which may be due to electronic transitions associated with the carboxylate anion and the nitryl cation bonds [15] and the percentage of transmission is about 10 %. From the spectrum, it is clear that the grown crystals are quite transparent in the wavelength region from 310 to 1100 nm. The resultant spectrum shows that the crystal has a very low absorbance in entire visible and IR region, which contributes to the crystal's higher resistance to laser induced damage. The title material is transparent in the entire visible region and this is one of the key properties of a nonlinear optical material. Hence Cadmium Picrate crystal can be used for nonlinear optical applications and in the second harmonic generation from the Nd: YAG lasers.

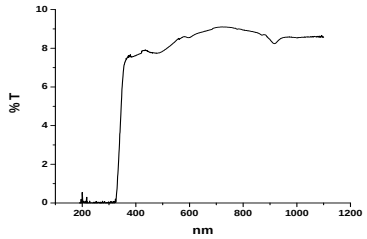

Fig-5: UV-Vis. Spectrum of Cadmium Picrate crystal

DETERMINATION OF OPTICAL BAND GAP

The dependence of the optical absorption coefficient with the photon energy helps to study the band structure and the type of transition of electrons [18]. The value of band gap energy is estimated from the graph plotted between hν and $(\alpha h\nu)^2$ by extrapolating the linear portion of the curve to zero absorption as shown in the Fig. 6. The absorption coefficient (α) is determined using Beer's law. The band gap energy, calculated is about 2.5 eV for the grown crystal. As a consequence of wide band gap, the crystal under study is relatively larger in the visible region [16]. The internal efficiency of the device also depends upon the absorption coefficient. Hence, by tailoring the absorption coefficient and tuning the band gap of the material, one can achieve the desired material which is suitable for fabricating NLO devices as per the requirements.

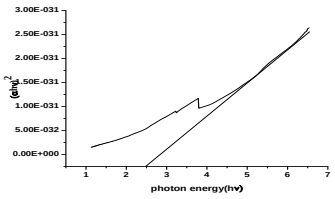

Fig-6: Plot of $(\alpha h\upsilon)^2$ Vs Photon energy of Cadmium Picrate crystal

3.6 MICROHARDNESS MEASUREMENTS - VICKERS MICRO HARDNESS TEST

The microhardness characterization is extremely important as far as the device fabrication is concerned. The grown crystals were subjected for microhardness measurement using a Vickers microhardness tester fitted with a diamond indenter. The Vickers micro hardness number H_v of the crystal is calculated using the relation

$$H_v = \frac{1.8544\,p}{d^2}\ kg/mm^2\ (or)\ pascal$$

Where P is the applied load in kg and d is the length of indentation impression in millimeter and 1.8544 is a constant of a geometrical factor for the diamond pyramid [17] and the load Vs H_v graph is shown in Fig.7. The Vicker's hardness number increases with the applied load. Work hardening coefficient 'n' is also calculated as 3.62 by using Mayers' relation by plotting a graph between log p versus log d and is shown in the Fig.8. The work hardening coefficient observed in the Cadmium Picrate crystal is greater than 1.6 and it ascertains that the grown crystal belongs to a soft material category.

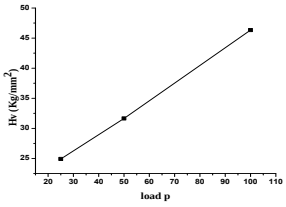

Fig-7: Vickers Hardness number with loads for Cadmium Picrate crystal

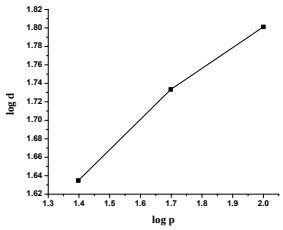

Fig-8: Graph between Log p Vs Log d for Cadmium Picrate crystal

3.7 DIELECTRIC MEASUREMENTS

Dielectric measurements for Cadmium Picrate single crystals have been carried out using HIOKI 3532-50 LCR HITESTER. The dielectric constant is calculated using the formula

$$\varepsilon' = C\,d / \varepsilon_o A$$

where C is the capacitance. d is the thickness, A is the area and ε_o is the absolute permittivity of the free space having the value 8.854×10^{-12} F/m. The imaginary dielectric constant (ε') is calculated using the relation

$$\varepsilon'' = \varepsilon' \tan\delta$$

where tanδ is the dielectric loss. Dependence of dielectric constant and dielectric loss of cadmium picrate crystals as a function log frequency [log (f)] at temperature 35 ˚C are displayed in the Figures 9 and 10. The obtained results suggest that the dielectric constant and loss strongly depends on the frequency of the applied field. It is observed from the results that both dielectric constant and loss is high at low frequencies and they decrease with increase in frequency. This may be due to the fact that at lower frequency space charge polarization is active and at higher frequencies the ionic and electronic polarizations are active [18].

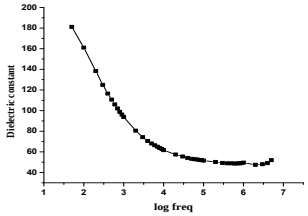

Fig-9: Dielectric constant of Cadmium Picrate crystal

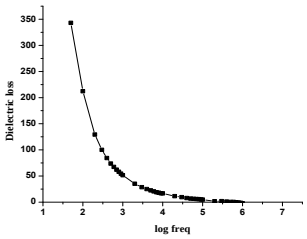

Fig-10: Dielectric loss of Cadmium Picrate crystal

3.8 SHG MEASUREMENTS

The fundamental beam of 1064 nm from Q-Switched Nd:YAG laser PAROLAB 170 Quanta ray has been used to test the SHG property of Cadmium Picrate crystal by the Kurtz and Perry technique [19]. The crystal has been ground into fine powder and densely packed in a micro capillary tube. The pulse energy of the 4mJ / pulse and pulse width 8 nS with a repetition rate of 10 Hz has been allowed to strike the sample cell. The fundamental beam has been filtered by using IR filter, a photo multiplier tube Philips Photonics has been used as a detector and KDP sample as a reference material. The output power intensity of Cadmium Picrate has been found to be 1.09 times that of KDP crystals. The green emission is confirmed the second harmonic generation in the grown crystal. Hence the crystal can be used for NLO device fabrications.

4. CONCLUSIONS

The single crystals of Cadmium Picrate has been successfully grown using slow evaporation methods. From the single crystal X-ray diffraction analysis the cell parameters are determined. The crystal size and the lattice strain are calculated using the powder X-ray datas. EDAX analysis confirms the presence of Cadmium in the crystal lattice of Cadmium Picrate. The presence of functional group is identified by FT-IR method. The optical behavior has been studied using UV–Vis analysis and found that there is no absorption between 310 nm and 1100 nm, which is the key requirement of NLO materials. The optical band gap (Eg) is also calculated as a function of energy. Mechanical hardness studies reveal that Vicker's hardness number increases as the load increases satisfying reverse indentation size effect which confirms the good mechanical stability of the material. The microhardness study also indicates that the grown crystal belongs to the soft material category. The dielectric studies prove that the samples possess a low dielectric constant and low dielectric loss values at higher frequencies which suggests that the sample possesses an enhanced optical quality with less defects. Its SHG efficiency has been tested by Kurtz and Perry using Nd:YAG laser as source and the output power intensity of Cadmium Picrate has been found to be 1.09 times that of KDP crystals.

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