SYNTHESIS, GROWTH, SPECTROSCOPY AND OPTICAL STUDIES ON NOVEL NONLINEAR OPTICAL MATERIAL: $Cd(I)_2$

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ABSTRACT

A new semiorganic cadmium iodide Cd(I)2 has been synthesizedn by slow evaporation method at room temperature. The lattice parameter values have been evaluated by single crystal XRD analysis for $Cd(I)_2$ crystal. The sharp well-defined peaks confirmed the crystalline nature of the material $Cd(I)_2$ crystal using Powder XRD analysis. A presence of functional groups in the synthesized compound were identified by FT-IR analysis. UV-visible analysis was carried out to determine the lower cut off wavelength and optical Band gap from UV-vis-NIR spectrum data. The SHG behavior was confirmed from the emission of bright green radiation (532nm), which confirms the good NLO material for several applications. The dielectric constant and dielectric loss studies were carriedout for $Cd(I)_2$ crystal.

Keywords: Semiorganic; XRD; FT-IR; UV and Dielectric.

5.1. INTRODUCTION

Extensive efforts were made in recent years to develop new inorganic, organic and semiorganic nonlinear optical materials that posses properties such as high threshold, wide transparency range and high nonlinear coefficient which make them suitable for frequency doubling [1]. Inorganic materials are much more nature in their application to nonlinear than the organic materials. The large nonlinearity inorganic material arises from the strong charge transfer and high polarizability [3,4]. Purely inorganic materials have excellent mechanical and thermal properties but posses relatively modest optical nonlinearity because of the lack of extended π- electron delocalization [5-7]. Many optically active organic amino acids are mixed with the inorganic salts I order to enhance their physical and chemical properties [8]. Currentlythe development of advanced new functional materials is of great interest. This is particularly true for non-centrosymmetric a material that is compound crystallizing ina space group with no centre of symmetry [9].

Non-centrosymmetric compounds are of great interest in material science and engineering; this is due to their interesting physical properties such as piezoelectricity, ferroelectricity especially for second harmonic generation in nonlinear optics [10]. Metal iodides had been extensively studied at the Bell laboratories for their NLO properties and also for their physical properties [11]. Iodate belongs to inorganic compound which posses (IO_3) amino group with pyramidial configuration like selenite's and tellurites [12]. Lone pair of I is disposed opposite apical iodide ion and provides polar distribution of the electron density in the group [13]. The presence of lone pair on iodine in the iodate group may induce non-centrosymmetric structure.

In this family, Li $(IO)_3$ is the only widely studied commercial iodate [14]. From the previous

research report a metal iodides have better relevant physicalproperties [15]. The investigation should be made on a non-centrosymmetric iodate crystals such as Li $(IO_3)_2$, $M(IO_3)_2$ and $Hg(IO_3)_2$. As a reference M $(IO_3)_2$, (M=Zn, Co, Mn, Mg, Cd, Hg) [16]. In the present investigation we concentrated on synthesis, growth, spectroscopy and optical studies on nonlinear optical material Cd $(I)_2$.

2. EXPERIMENTAL PROCEDURE

2.1. Synthesis and Solubility

Analar reagent (AR) grade of potassium iodide KI and Cadmium chloride $(CdCl_2)$ in the stoichiometric ratio 2:1 were used for synthesis. The chemical reactionis,

$$\mathbf{2(K\,I) + Cd\,Cl_2 \rightarrow Cd\,(I)_2}$$

The calculated amount of potassium iodide and cadmium chloride were dissolved in 100ml of de-ionised water and stirred well using a magnetic stirrer for about 6 hours. The prepared solution was allowed to dry at room temperature and the salts were obtained by slow evaporation technique. The purity of the synthesized salt was further improved by successive recrystallization process. The solubility of the synthesized salt was carried out atvarious temperature 35-55 ºC in 5 ºC intervals by dissolving the solute in de-ionized water in an airtight container maintained at constant temperature with stirring. After attaining saturation, the equilibrium concentration of the solute was analyzed gravimetrically. The same procedure was repeated and the solubility curve for different temperature was drawn. Figure 1 shows the solubility curve for Cd $(I)_2$ in aqueous solution.

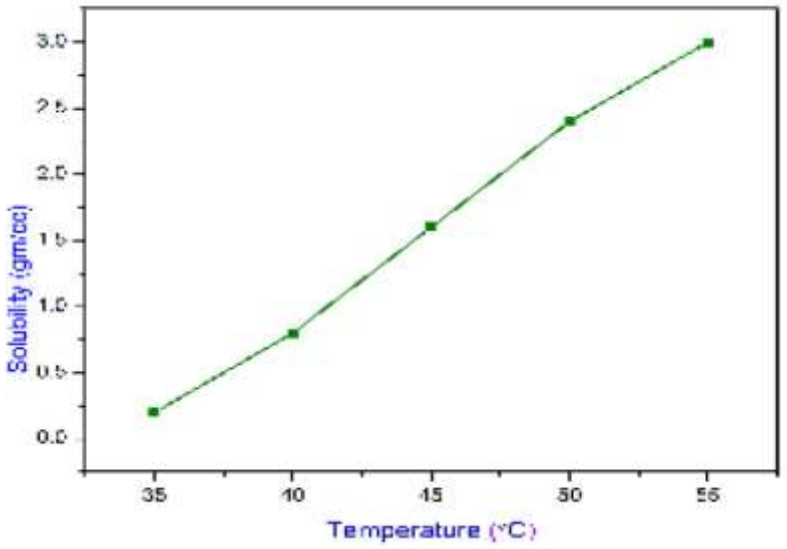


Figure 1. Solubility curve of Cd $(I)_2$ crystal

2.2. Crystal Growth

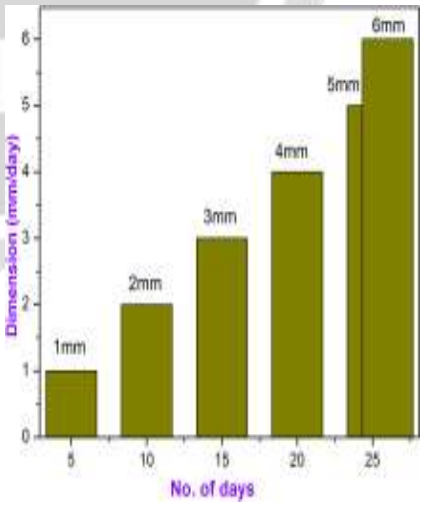
The calculated amount of recrystallized salt of Cd(I)2 were dissolved in 100ml of de-ionized water using magnetic stirrer and the solution were saturated at 40 ºC. Then, the solution was kept in a constant temperature bath controlled to an accuracy of ±0.01 ºC. The solution was maintained at 40 ºC for 2 days in order to attain homogeneity. After that optical quality seed crystal obtained by slow evaporation method was suspended in the growth solution. The temperature was reduced initially at the rate of 0.1 ºC per day and subsequently 0.2 ºC per day as the growth progressed. After the completion of growth process, over a typical period of 35 days well developed crystal of size about

06x05x03 mm^3 was harvested. The grown crystal of Cd $(I)_2$ is shown in figure 2 and the growth ofcrystal are shown in table 1.

Figure 2. As grown crystal of Cd (I)2

Table 1. Optimized grow conditions of Cd (I)2

Techniques	Slow evaporation
Solvent	De-ionized water
potassium iodide and Zinc chloride	2:1 molar ratio
Period of growth	35 days
Crystal size	6x5x3 mm^3



3. CHARACTERIZATION TECHNIQUES

3.1. Single crystal X-ray Diffraction:

The grown Cd (IO3)2 crystals were subjected to single crystal x-ray diffraction studies using ENRAF NONIUS CAD4 automatic x-ray diffractometer. The x-ray diffraction study on grown crystal was used to confirm the quality, structure and identification of cell parameters. It is found that cell parameters are a=11.137Å, b=5.271 Å, c=11.142 Å, and volume V= 654.07 $Å^3$ and the crystal Cd $(I)_2$ belongs to Trigonal crystal system.

3.2. Powder X-ray Diffraction:

The recorded XRD pattern is shown in figure 3 which was analyzed by using powder X-ray diffraction studies with Cukα (λ=1.5406 Å) radiation. The powdered sample was scanned in the range 10-80 ºC at a scan rate of 1º per minute. In the powder XRD pattern well defined Bragg's peaks are observed which reveals that the grown crystal of Cd $(I)_2$ has highly crystalline nature.

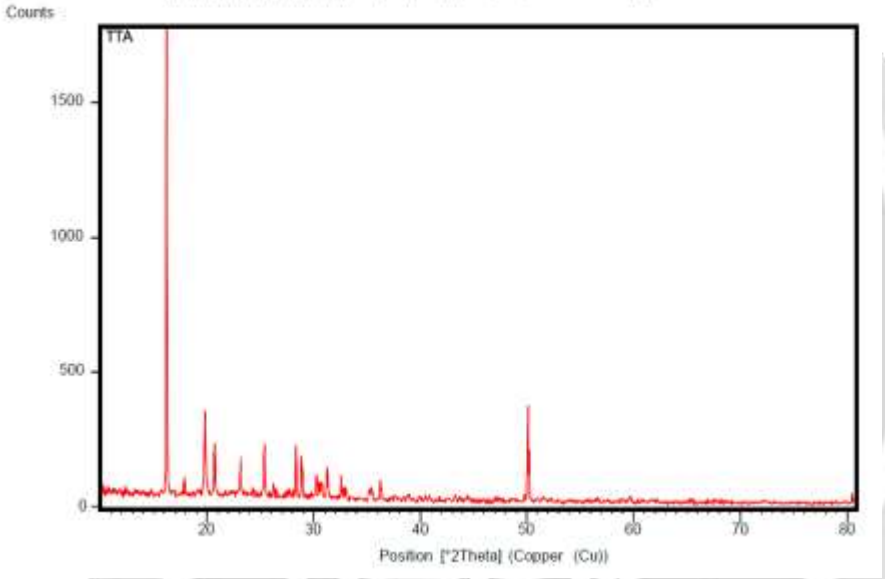


Figure 3. Powder XRD pattern of grown Cd $(I)_2$ crystal

3.3. Fourier Transform Infrared (FTIR) spectroscopy study:

In order to analyze the synthesized compound qualitatively for the presence of functional groups in the molecule, the FTIR spectrum is recorded between 500- 4000 cm-1 using KBr pellet technique by Brukker IFS 66V Fourier transform infrared spectrometer. The spectrum obtained is shown in figure 4. A sharp peak observed at 3819 and 3525 cm-1 corresponds to OH stretching. The H bonded OH stretching is observed at 2995 cm-1. The peaks at 1621 and 1088 cm-1 is due to bendind and rocking vibration. The OH out of plane bending was observed at 947 cm-1. A sharp peak at 754 cm-1 assign to both Cd-O and I-O vibrations. The I-O stretching and bending are observed at 663 and 524 cm-1. The characteristic IR bands for different molecular groups present in the $Cd(I)_2$ have been identified and their assignments are given in table 2.

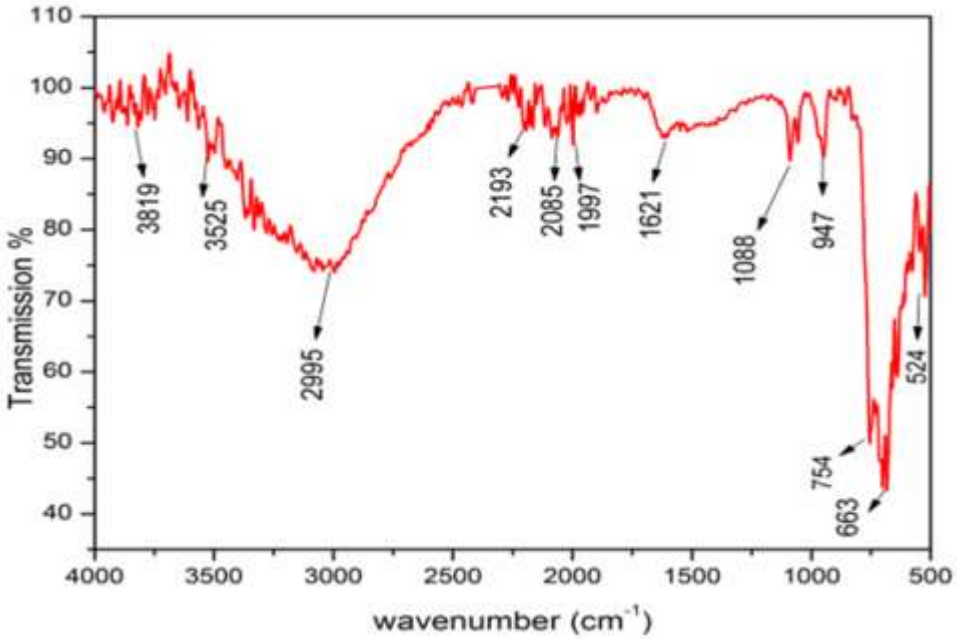


Figure 4. FTIR spectrum of Cd(I)2 crystal

Table 2. Assignments of IR band frequencies (cm^{-1}) for $Cd(I)_2$

Wavenumber cm^{-1}	Assignments
3819,3525 cm^{-1}	OH stretching
2995 cm^{-1}	H bonded OH stretching
1621cm^{-1}	Bendind vibration
1088 cm^{-1}	Rocking vibration
947 cm^{-1}	OH out of plane bending
754 cm^{-1}	Cd-O and I-O vibrations
663 cm^{-1}	I-O stretching
524 cm^{-1}	I-O bending

3.4. Linear optical study

The optical absorption spectrum of Cd (I)2 crystal was recorded in the range 200-1000 nm using Perklin Elmer Lambda 35 UV/VIS spectrometer. Figure 5, shows the optical absorption spectrum of $Cd(I)_2$ crystal. From the spectrum, it is evident that the grown crystal has a very low cutoff wavelength of 297 nm. There is no absorption in the visible region. This lower cutoff is well suited for SHG and other application in green region.

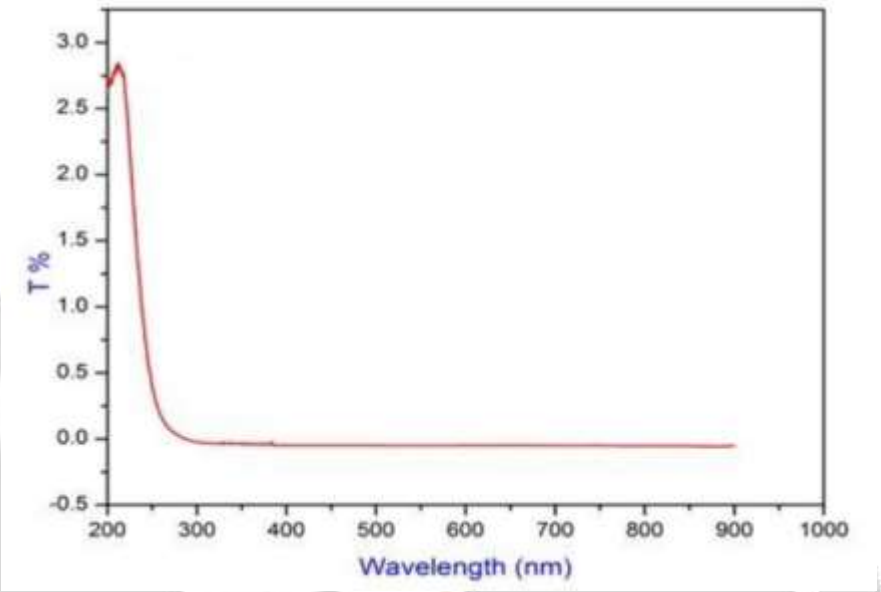


Figure 5. Optical absorption Spectrum of Cd (I)2 crystal

3.5. Determination of optical band gap (Eg)

The dependence of optical absorption coefficient on photon energy helps one to study the band structure and the type of transition of electrons [17]. The optical absorption coefficient (α) was calculated from transmittance using the following relation.

$$\alpha = \frac{1}{d}\log\left(\frac{1}{T}\right)$$

Where T is the transmittance and d is the thickness of the crystal. As a direct band gap material, the crystal under study has an absorption coefficient (α) obeyingthe following relation for high photon energies (hν).

$$\alpha = \frac{A(h\nu - Eg)^{\frac{1}{2}}}{h\nu}$$

Where Eg is the optical band gap of the crystal and A is a constant. The plot ofvariation of $(\alpha.h\nu)^2$ versus hν is shown in figure 6. Optical band gap was evaluatedby extrapolation of the linear part [18]. The band gap (Eg) is found to be 5.1 eV. As a consequence of wide band gap, the grown crystal has large transmittance in the visible region [19].

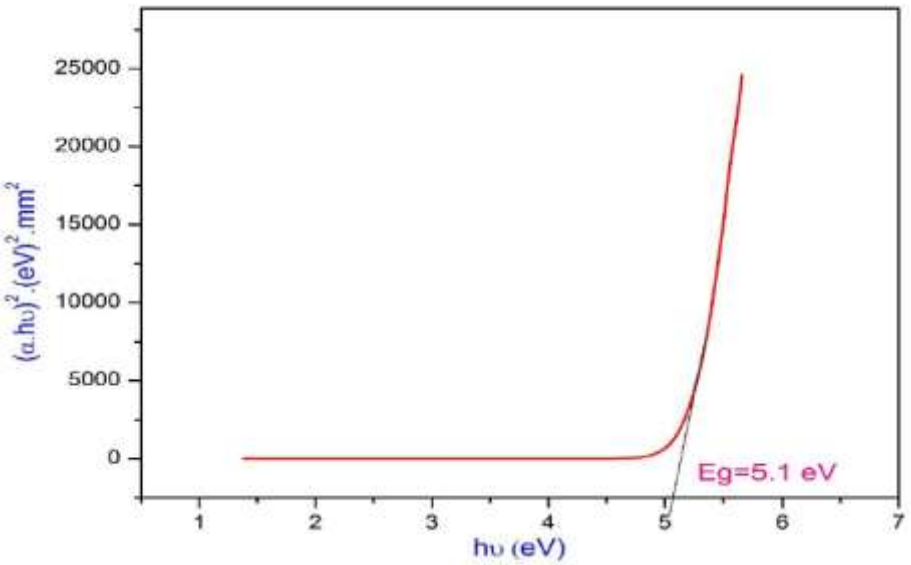


Figure 6. Tauc's plot of $Cd(I)_2$ crystal

3.6. Nonlinear optical study

The second harmonic generation (SHG) of the grown sample was confirmed by Kurtz powder technique. The powder sample of $Cd(I)_2$ crystal was packed in a triangular cell and kept in a cell holder. The fundamental beam of 1064 nm from Q- switched Nd:YAG laser is used to test the second harmonic generation property of $Cd(I)_2$ crystal by using Kurtz technique. The output from the Q-switched laser as focused into the crystal. The emission of green radiation from the $Cd(I)_2$ crystal confirms the SHG in the grown crystal, which evident that the grown $Cd(I)_2$ crystal is a suitable material for nonlinear optic (NLO) applications.

3.7. Dielectric Studies

Dielectric properties are correlated with the electro-optic property of the crystals [21]. The capacitance (Ccrys) and dielectric loss (tan δ) were measured using the conventional parallel plate capacitor method with the frequency range 50 Hz to 1 MHz using the Agilent 4284A LCR meter at various temperatures ranging from 313 to 333 K. A good quality as grown crystal of 2 mm thickness was electroded on either side with graphite coating to make it behave like a parallel plate capacitor. The observations were made while cooling the sample. Air capacitance (Cair) was also measured.

The dielectric constant of the Cd(I)2 crystal was calculated using the relation:

$$\varepsilon_r = \frac{C_{crys}}{C_{air}}.$$

The frequency dependence of the dielectric constant and dielectric loss at different temperatures is shown in Figure 7 and 8. The dielectric constant decreases with increasing frequency and finally it becomes almost a constant at higher frequencies for all temperatures. It is also indicating that the value of dielectric constant increases

with increase in temperature. The same trend is observed in the case of variation of dielectric loss with frequency at different temperatures. The dielectric constant of materials is due to the contribution of electronic, ionic, dipolar and space charge polarizations which depend on the frequencies [22]. The space charge polarization is generally active at lower frequencies and high temperatures. At higher frequencies, the decreased dielectric constant could be due to the reduction in the space charge polarization. The dielectric constant and dielectric loss studies of $Cd(I)_2$ crystal establish the normal behavior. The characteristic of low dielectric constant and dielectric loss with high frequency for a given sample suggests that the sample possesses enhanced optical quality with lesser defects [23] and this parameter is of vital importance for various nonlinear optical materials and their applications.

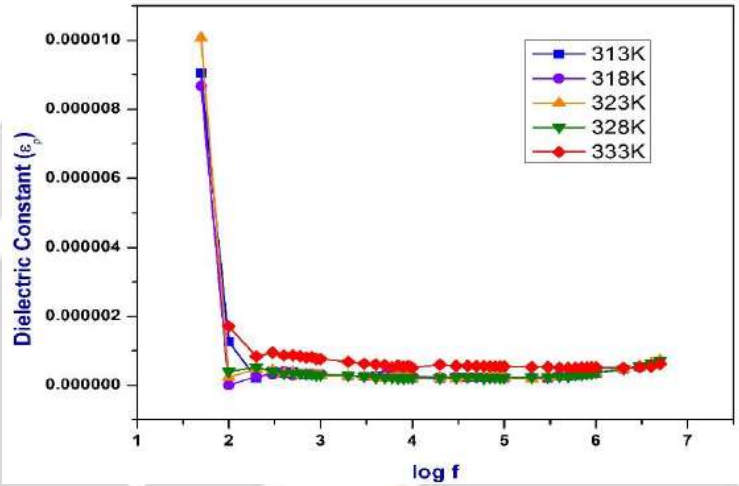


Figure 7. Variation of dielectric constant with log frequency for Cd(I)2 crystal

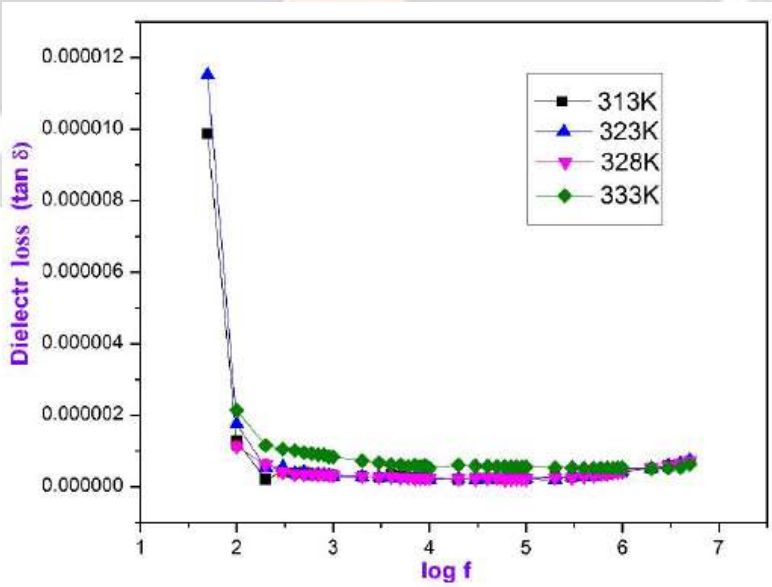


Figure 8. Variation of dielectric loss with log frequency for Cd(I)2 crystal

4. CONCLUSION

A new NLO material Cd(I)2 has been synthesized and crystals were grown by slow evaporation method. The lattice parameter values have been evaluated by single crystal XRD analysis. From the XRD analysis the crystal Cd(I)2belongs to trigonal system. The sharp well-defined peaks confirmed the crystalline nature of the material. The functional groups have been confirmed from FT-IR analysis. UV- visible analysis was carried out to determine the lower cut off wavelength at 297 nm and also optical Band gap (Eg=5.1eV) were determined from UV-vis-NIR spectrum The SHG behavior was confirmed from the emission of bright green radiation (532nm). So it is a good NLO material for several applications. The dielectric constant and dielectric loss studies of Cd(I)2 crystal establish the normal behavior.

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