IOSR Journal of Engineering (IOSRJEN) www.iosrjen.org
ISSN (e): 2250-3021, ISSN (p): 2278-8719
Vol. 08, Issue 9 (September. 2018), ||V (V) || PP 52-61

A Study on the Synthesis, Structural, Spectral and Optoelectronic Properties of Pure and Sodium Ion Incorporated Cadmium Oxalate Nonlinear Optical Single Crystals

F. Daisy Selasteen[1], S. Alfred Cecil Raj[2]
[1]P. G and Research Department of Physics, Bishop Heber College, Tiruchirappalli, TamilNadu, India.
[2]School of Physics, St. Joseph's College, Tiruchirappalli, TamilNadu, India.
Corresponding Author: F. Daisy Selasteen

Abstract: Cadmium oxalate $CdC_2O_4.3H_2O$ (CdOx) and sodium cadmium oxalate $[Na_4Cd_2 (C_2O_4)_4.4H_2O]$ (NaCdOx) were grown as single crystals using single diffusion silica gel technique and the conditions influencing the size, shape and quality were optimized at ambient temperature. Single crystal XRD was carried out to analyze the crystal structure. A monoclinic system with the space group $P_{21/n}$ was revealed using full matrix least square technique employing the SHELXL program. The results of the structural analysis indicate that the complex formed by the Na-O and Cd-O coordination bonds explore a two-dimensional network structure which was further linked by O-H···O hydrogen bonds to give a three-dimensional structure. The vibrational modes of oxalate ligand functional groups were identified by the FTIR spectroscopy. The wide transmittance and the calculated band gap energy $E_g = 4.06$eV and 4.25eV of NaCdOx and CdOx crystals from the UV spectrum proved that they were good non-linear optical materials. DSC spectrum showed the thermal stability, crystallization and the phase transition temperatures of the NaCdOx and CdOx crystals. The Photoluminescence spectrum of NaCdOx crystal showed the strong and efficient red emission around 302 nm identified this promising emission can be effectively used for optical amplification. The dielectric studies revealed that the electrical conductivity of the as-grown samples lies between the semiconductors and insulators confirmed that they are suitable nonlinear optical materials for the fabrication of optoelectronic devices.

Keywords: $[Na_4Cd_2 (C_2O_4)_4.4H_2O]$ and $[CdC_2O_4.3H_2O]$ crystal structure, crystal growth from gel, optical and electrical properties, nonlinear optical materials.

Date of Submission: 29-09-2018 Date of acceptance: 14-10-2018

I. INTRODUCTION

The oxalate compound is involved in constructing a large variety of molecular assemblies and frameworks by combining suitable metal ions in the crystal lattice. It can perform as a mono dentate, bidentate, tridentate or tetra dentate donor ligand and can yield chains, layers or three-dimensional networks with metal centers. Remarkably, oxalate is often encountered as a bidentate ($C_2O_4^{2-}$), metal coordination complexes. Water molecules bound metal ions or weakly fused to the metal oxalate frameworks have a greater influence on structural architectures of one, two or three dimensions [**1, 2**]. The combination of alkali mixed heavy metal elements with oxalate ions produces new compounds which are scientifically and technologically interesting and merit special attention because of their many fascinating structural, dielectric, thermal and optical [**3,4]** properties which are utilized widely in their use in transducers and optoelectronic industries [**5**].

The optical conductivity in oxalate salts is due to the hydroxyl and metal-oxygen groups of the metal-oxalate matrix [**6**]. Optimized higher order optical conductivity on some inorganic centro symmetric bimetallic oxalate and chloride have been suggested their potentiality for luminescent and nonlinear optical applications [**7, 8**].

The oxalic acid derived metal (as Fe, Na, Cd, Zn, and Cu) complexes, are mostly ionic bonded, high melting points and high degree of chemical inertness have been potentially utilized in various applications, such as molecular magnets [**9**], luminescence materials [**10**], and sensors [11]. The effect of impurity plays a vital role in deciding the growth and physical properties [12] of the metal oxalates. In ionic doping, Na^+ is an important metal ion with defined thermal stability and ionic conductivity properties and is a versatile dopant. Further, the presence of the Na^+ ion in the metal oxalate structure is utilized the bimetallic dicarboxylate complexes in the optoelectronic applications [13].

The structural and thermal properties of a sodium cadmium oxalate crystal using the hydrothermal synthesis technique $[Na_4Cd_2 (C_2O_4)_4.4H_2O]$ have been reported [14]. However, there are very few reports on the bimetallic oxalate crystal. Hence, in the present study, an attempt has been made to grow sodium doped cadmium oxalate crystals by a silica gel technique using single diffusion method. In order to prove the bimetallic material (NaCdOx) is optically good, thermally and electrically active, the title compound has been subjected to various characterizations such as single crystal XRD, FTIR, UV-Vis-NIR, DSC, and dielectric studies.

II. EXPERIMENTAL

2.1 Materials and methods

The high-purity elements such as cadmium chloride (LOBA Chemie, 99.95 % Assay), sodium chloride (LOBA Chemie, 99.95 % Assay), oxalic acid (LOBA Chemie, 99.99 % Assay), and sodium metasilicate (LOBA Chemie, 99.9 % Assay) with AR grade were used as the starting materials in the single diffusion chemical reaction method at the ambient temperature. The lattice parameters of the grown single crystal were determined by adopting ENRAF NONIOUS CAD4 X Ray diffractometer with MoKα (0.71073 Å) radiation and it provided the precise determination of the unit cell dimensions of the grown crystal. The structure of NaCdOx crystal was solved by the direct method and refined by the full matrix least square technique employing the SHELXL program.FTIR spectrum of NaCdOx was recorded using a Perkin-Elmer RXI Spectrometer by KBr pellet technique in the wave number range 400-4000 cm^{-1}. Optical absorbance and transmittance are very powerful method to determine the energy gap and particle size as well as the optical properties of the samples. In order to estimate the optical transparency in the 190-1100 nm region of the electromagnetic spectrum, the linear optical study was carried out for the title compound of thickness approximately equals to 1mm employing PERKIN ELMER LAMDA 35 model spectrometer. The study of optical transmittance and particularly the absorption edge is very useful to find the optical constants and provide the key to investigate the optical properties.

Thermal studies were carried out in nitrogen atmosphere using the instrument SDT Q600 V20.9 in the temperature range of 20°C to 1100°C. The weight of the NaCdOx and CdOx crystals used for the measurement were from 3 to 4 mg and the heating rate was 10° C/min under nitrogen medium. DSC spectrum was used to study the thermal behavior of the as-grown NaCdOx and CdOx crystals whenever it experienced a physicochemical change such as melting or transition from one crystalline to another or whenever it reacted chemically, the heat was either liberated or absorbed. Photoluminescencestudies are a non-destructive tool to carry out the luminescence behavior of the grown optical material. Photoluminescence properties were investigated in solutions at room temperature by Cary Eclipse Spectro Fluro meter. The recorded emission spectrum of present samples was taken in the range of 200 to 400 nm in the excitation wavelength of 225 nm. A HIOKI 3635 model LCR meter was used to measure the capacitance, dielectric loss (tan δ), and resistance of the present grown crystal as a function of frequency (range 30-95^{0}C). A small cylindrical furnace (20cmx20cmx20cm) whose temperature was controlled, by the Euro Therm temperature controller (0.01°C) was used to house the sample

2.2Synthesis and growth of Na_4Cd_2 (C_2O_4) $_4.4H_2O$

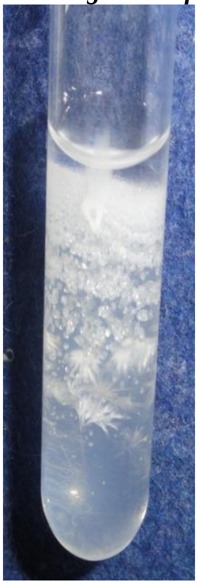

Figure 1(a)

Figure 1ba)

Figure 2(a)

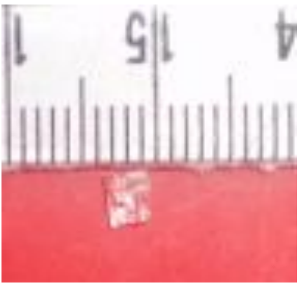

Figure 2(b)

Figure.1 (a): Growth of NaCdOx crystal by the silica gel method.
Figure.1 (b): Growth of CdOx crystal by the silica gel method.
Figure.2 (a): Morphology of CdOx crystal grown by a silica gel method.
Figure.2 (b): Morphology of NaCdOx crystal grown by a silica gel method.

The sodium cadmium oxalate chelate was prepared by the slow addition of cadmium chloride (2 mmol in 10 ml of water) to a freshly prepared silica hydro gel [addition of sodium Metasilicate solution (1.03 specific gravity) to oxalic acid (2 mmol in 10 ml of water)], maintaining the pH at 4.5 and left for a few days at room temperature for crystallization of the complexes. When sodium Metasilicate goes into a solution, mono silisic acid is expected to be produced [**15**] according to the following reaction (1),

$2Na_2SiO_3+6H_2O\rightarrow 2H_4SiO_4+4NaOH$ (1)

This sodium hydroxide is expected to react with oxalic acid, diffusing in a gel from the supernatant solution and forming sodium mixed cadmium oxalate crystals by the following reaction (2),

$4NaOH+4H_2C_2O_4.\ H_2O+2CdCl_2\rightarrow [Na_4Cd_2\ (C_2O_4)\ _4.4H_2O]\ +4HCl.$ (2)

After passing ten days, the $[Na_4\ Cd_2\ (C_2O_4)\ _4.4H_2O]$ crystal was obtained as suitable single crystal for X-ray diffraction analysis. The preparation and growth of $CdC_2O_4.3H_2O$ (CdOx) in the silica gel medium were doing similar to the method which has been reported [**16**] already.

Good quality crystals were found at the bottom of gel column since the availability of the ions has been just sufficient for the growth of crystals. Within the gel pH range from 4.5 considered, crystallization of CdOx was favored the Liesegang ring formation and below that isolated nucleation sites were observed by the controlled nucleation density was shown in **Fig.1 (a),** whereas in the Sodium cadmium oxalate, the maximum number of crystals with dendrite shaped colorless crystals were observed near the interface was shown in **Fig.1 (b)**.Typical morphological photographs of as-grown crystals were displayed in **Fig. 2(a) and (b).**

.

III. RESULTS AND DISCUSSION

3.1 X-ray diffraction Analysis

Single crystal X-ray diffraction analysis of the grown cadmium (II) crystals has been carried out to identify the cell parameters using an ENRAF NONIUS CAD 4 automatic X-ray diffractometer. In the structure of sodium cadmium oxalate dihydrate $[Na_4Cd_2\ (C_2O_4)\ _2\ 4H_2O]$ n complex as exhibited in **Fig.3**, the repeat unit has two oxalate groups, one cadmium (II) atom, two sodium atoms and four water molecules. The oxalate ligand has an inversion center of the midpoint of the C-C bond. In the pure cadmium oxalate trihydrate $[CdC_2O_4.3H_2O]$ complex about **Fig.4**belongs to the triclinic crystal system to the P-1 space group of cadmium atom lying on a center of symmetry is coordinated by eight oxygen atoms in which four of the oxalate units and water from the four molecules. These results are well agreed with the previously reported results [**17**] of gel grown cadmium oxalate crystals.

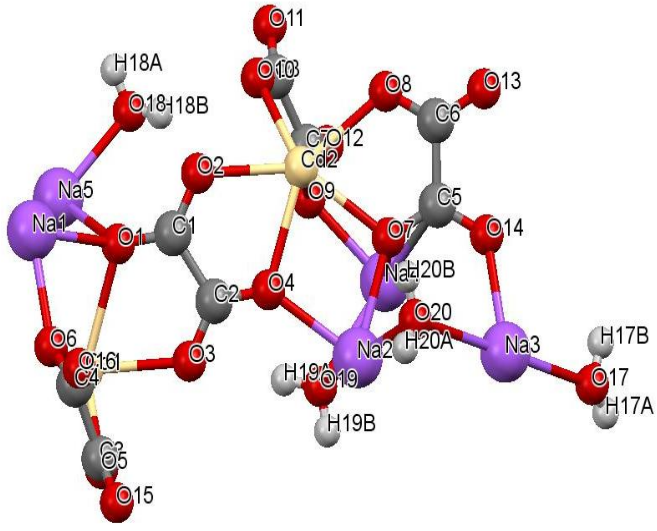

Figure.3. Atoms arrangement of NaCdOx

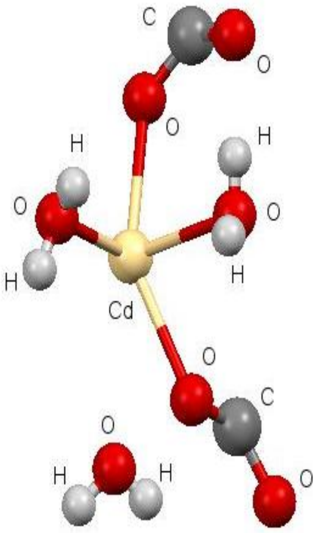

Figure.4.Atoms arrangement of CdOx.

The fundamental features of the obtained structure are as follows. The frame structure of NaCdOx is built up by the linkages between the Cd, Na and the oxalate units with each Cd bound to eight oxygen atoms forming the cadmium is a dodecahedron arrangement with respect to the oxygen atoms. The crystal structure and refined parameters of NaCdOx and CdOx are shown in **Table 1**.The eight oxygen atoms from the oxalate units and the water molecules bind the cadmium atom build the repeated binding units of the NaCdOx crystal into the polycrystalline material [**18**]. In this polymeric packing, the framework stability is maintained by an extensive hydrogen bond network involving all O atoms of sodium cadmium oxalate anion. The H_2O molecules in the observed structure of $[Na_4Cd_2\ (C_2O_4)\ _4.4H_2O]$ n, form the O–H…O hydrogen bonds in which the resonance assisted strong hydrogen bonds (O-H) is attributed to the high optical properties of the bimetallic NaCdOx crystal were exactly established with the reported outcomes [**19**].

Table1: Calculated lattice parameters for $[Na_4Cd_2\,(C_2O_4)\,_4\,4H_2O]$ and $[Cd\ (C_2O_4)\ 3H_2O]$ crystals using full matrix least square technique employing SHELX program by single crystal XRD studies**.**

Empirical formula	(C4 H4 Cd Na2 O10)$_n$	(C2 H6 Cd O7) n
Formula weight	812.508	254.47
Temperature	273 (2) K	293 (2) K
Wavelength	0.71073 A	0 .71073 Å
Crystal system	Monoclinic	Triclinic
Space group	P21/n	P-1
Unit cell dimensions	a = 12.8566 (6) Å : α= 90° b = 11.4338 (5) Å: β= 113.07° c = 14.1144 (6) A: γ= 90 °	a=5.9944 (2) Å: α= 74.63° b=6.6531 (2) Å. β= 4.28°. c=8.4731 (3) Å: γ= 81.04°.
Volume	1908.86 (15) Å^3	312.377 (18) Å^3
Z	8	2
Calculated density	2.425 Mg/m^	2.705 Mg/m^3
Absorption coefficient	2.578 mm^-1	3.479 mm^{-1}
F (000)	14240.	244
Crystal size	0.30 x 0.25 x 0.20 mm^3	0.150 x 0.100 x 0.100 mm^3
Theta range	1.82 to 26.00°	2.569 to 28.999°.
Limiting indices	13<=h<=15, -14<=k<=14, -17<=l<=16	-8<=h<=8, -9<=k<=9, -11<=l<=11
Reflections collected / unique	19233 / 3752 [R (int) = 0.0234]	1664 [R (int) = 0.0231]
Completeness to theta	=26.00° 100.0 %	= 25.242° 100.0 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
T (Max. and Min.)	0.664 and 0.481	0.68 and 0.56
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3752 / 12 / 343	1664 / 0 / 116
Goodness-of-fit on F^2	1.130	1.161
Final R indices	R1 = 0.0159, wR2 = 0.0405	R1 = 0.0106, wR2 = 0.0270
R indices (all data)	R1 = 0.0168, wR2 = 0.0413	R1 = 0.0108, wR2 = 0.0271
Extinction coefficient	0.00265 (11)	0.0473 (15)
Largest diff. peak and hole	0.443 and -0.332 e. Å^{-3}	0.549 and -0.350 e. Å^{-3}

3.2 FTIR Spectral analysis

The FTIR spectral analyses for CdOx and NaCdOx crystals were shown in the **Fig.5**.The presence of broadband of the wave number range of 3100–3500 cm^{-1} was showed the vibration spectra of O-H stretching frequencies of water molecule [**20**]. A strong band of 1619.9 cm^{-1} and 1613.7 cm^{-1} was assigned to ν (C=O) vibration in NaCdOx and CdOx crystals providing a strong evidence for the ligand coordination around cadmium ion in the deprotonated oxalate form [**21**]. The existences of free and coordinated C–O bonds were generated two pairs of anti-symmetric and symmetric ν (COO) stretching vibrations. The projected assignment ν_{as} (COO) > ν_s (COO) was in good agreement with the results of an important number of natural oxalates [**22**].

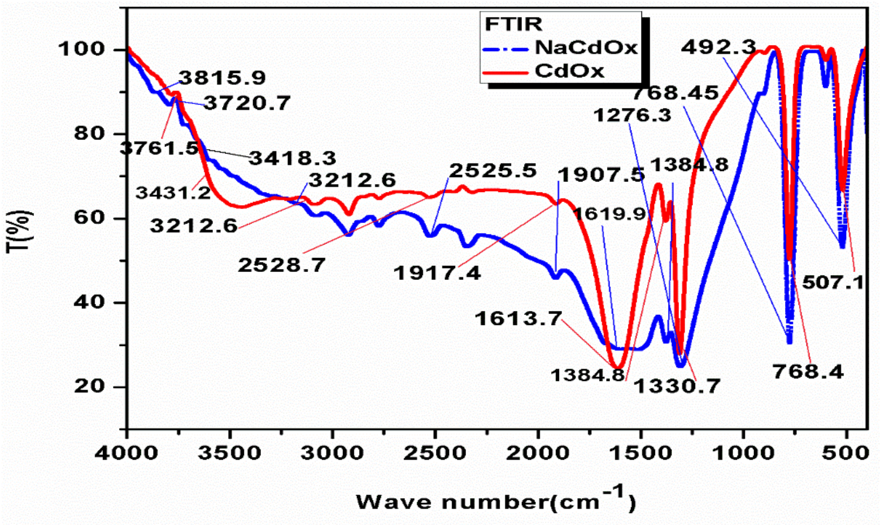

Figure.5. Oxalate-Ligand functional group assignments of NaCdOx and CdOx crystals by FT-IR spectra.

Table 2: various modes of vibrations of oxalate-ligand functional group Assignments of NaCdOx and CdOx crystals by FT-IR spectroscopy. Band positions in (cm−1).

NaCdOx	CdOx	Assignment
3720.7m	3761.5m	OH, asymmetric stretching vibration of H_2O
3418.3w	3431.2w	OH, symmetric stretching vibration of H_2O
3212.6w	3212.6w	OH, symmetric stretching vibration of H_2O
2525.5 vw	2528.7vw	COO- asymmetric stretching
1907.5w	1917.4w	COO- asymmetric stretching
1619.9vs	1613.7vs	C=O asymmetric stretching
1384.8w	1384.8w	CO symmetric stretching and O-C=O deformation stretching
1276.3vs	1330.7vs	CO symmetric stretching C-C symmetric stretching
768.45vs	768.4vs	O-C=O deformation stretching
492.3vs	507.1vs	M-O Metal -Oxygen bonding

Vs.-very strong; s-strong; m-medium; w-weak; vw-very weak;

The ν (O–H), ν $(COO)^-$ asymmetric stretching vibrations and one of the O-C=O deformation modes of vibrations were found at 3720.7 cm^{-1}, 3418.3 cm^{-1}, and 1384.8 cm^{-1} which were standard for the optical and electrical properties [**23, 24**] of the NaCdOx crystal. The bands below 800cm^{-1} was due to the metal oxygen (M-O) bands. The charge transfer (CT) of electron delocalization interaction, which is caused by the transfer of electrons from occupied Na-O to vacant Cd-O, and the higher order coupled interactions. The number of absorption bands of the lower wave number region (<800 cm^{-1}) of sodium doped CdOx crystal was revealed the incorporation of sodium ions in the CdOx crystal lattice which formed additional metal – oxygen (Na-O) bonding. In the case of sodium cadmium oxalate crystal, the missing of peaks at the ranges of1300 to 2000cm^{-1} was due to the effect of sodium incorporating into the cadmium oxalate structure. **Table4** summarizes the FTIR results of the pure cadmium oxalate and sodium cadmium oxalate crystals.

3.3 DSC spectral studies

The DSC spectrum of NaCdOx and CdOx crystal was shown in **Fig.6**. The endothermic peaks at 120.25°C and 134.86°C of CdOx and NaCdOx crystals were referred to the transition of amorphous to crystalline solid showed a peak of the DSC signal was known as the crystallization Temperature (T_C). A large exothermic peak was clearly seen on the DSC curve of NaCdOx and CdOx crystals at 348.59°C and 345.34°C with an onset temperature at 341.03°C and 338.01°C was represented as a phase transition from solid to gaseous state which informed the discharge of CO and CO_2 gas molecules due to the redox process which converted the hydrated crystalline $Na_4Cd_2(C_2O_4)_4$ salt into $2Na_2O.CdO_{(s)}$, $4CO_{(g)}$ and $4CO_{2\,(g)}$ [**25**]. The liberation of $\frac{1}{2}O_2$ gas molecules with the stable end product of sodium cadmium oxide ($2Na_2CdO$) crystal during the third stage that extends up to the temperature range of 450ºC-750ºC. The difference in the transition temperature between the cadmium oxalate and sodium cadmium oxalate salts may be caused only by the influence of sodium ion in the structure of NaCdOx crystal.

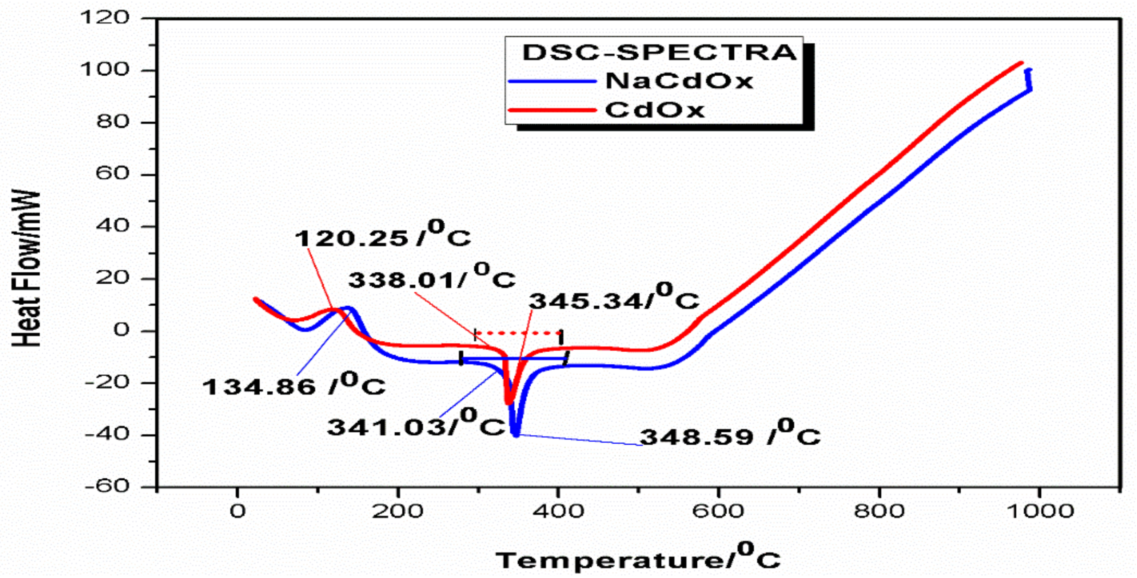

Figure.6. Observation of crystallization and phase transition temperatures of NaCdOx and CdOx crystals

•

3.4. UV- Transmittance spectral studies

From the UV transmission spectrum, the lower cutoff wavelength for NaCdOx and CdOx crystals was found to be 303.5 and 289 nm respectively was shown in **Fig.7 (a)** and **(b).** This special characteristic lower cutoff peaks at 303.5 and 289 nm for NaCdOx and CdOx crystals agreed to the n-π* transition due to a ligand-to-metal (M-O) charge transfer [**26**]. Apart from the n-π* transition, the transmission edge was established to be 95% of pure cadmium oxalate crystal and 98.4% of sodium cadmium oxalate crystal in the wavelength region 245nm-1200nm was attributed by the intermolecular resonance assisted hydrogen bonds of the as-grown crystal. Hence, the 98% of excellent transparency of NaCdOx crystals in UV-Vis-NIR region signifying that it could be used as a predominant material for exhibiting optoelectronic device fabricating applications [**27**, **28**].

The relation between the refractive index (n) and the energy gap (E_g) through the improved form of T. M Moss *etal.* and C. RamachandraRajaa, *et al.*, [**29, 30**] were given by the expression (1),

$E_g e^n = 36.3$ (1)

This relation is suitable for the energy gap greater than 0 eV. Dispersion is an important property for optical activity of the as-grown samples. Further studies on the refractive index (n) and reflectance (R) of the crystals are calculated by using the expression (2),

$\mathbf{R} = \left(\frac{\mathbf{n-1}}{\mathbf{n+1}}\right)^{\mathbf{2}}$ (2)

In the high photon energy region, the energy dependence of absorption coefficient was given by the equation (3),

$\alpha = \frac{2.303}{t} \log \frac{1}{T}.$ (3)

Table 3: Calculated optical parameters of as-grown NaCdOx and CdOx crystals

Compound	**Wavelength (nm)**	**Energy gap (eV)**	**Ref. Index (n)**	**Reflectance (R)**
NaCdOx	303.05	4.06	2.190	0.13915
CdOx	289	4.25	2.145	0.1325

Where ‘T’ is the transmittance and‘t’is the thickness of the present samples. Absorption coefficient ‘α’ suggests the occurrence of a direct band gap between the crystals which obeys the following equation (4), for high photon energies (hυ) [**31**],

$(\alpha h\gamma)^2 = A\ (E_g - h\nu).$ (4)

where ‘α’ is the absorption coefficient, ‘h’ is the Plank’s constant, ‘A’ is an absorbance, and ‘υ’ is the frequency of the incident photon and ‘E_g’ is the optical band gap. The calculated band gap energy, high value of refractive index and low value of reflectance from the given **Table 3** shows the as-grown crystals have wide transparency window and more transparency to transmit the light from 250 to 1100nm.As a result, the title crystals have been shown to be the useful material for the nonlinear optical applications.

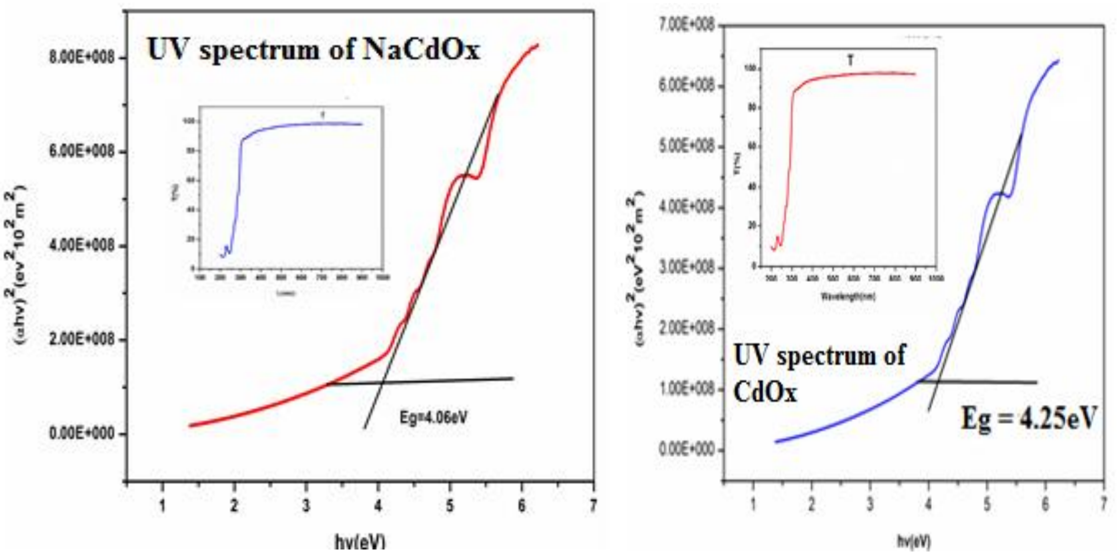

Figure.7 (a) Figure.7 (b)

Figure.7 (a). Nonlinear optical spectrum of NaCdOx **Figure.7 (b).** Nonlinear optical spectrum of CdOx

3.5. Photoluminescence analysis

The observed first broad peaks at 302 nm and 311nm of the PL emission spectrum in the **Fig.8** resembled to the π-$\pi^*$and n-π^*transitions of the NaCdOx and CdOx crystals proves the charge transfer (CT) interaction in their metal ligand units. This showed that they are good nonlinear optical materials. The maximum intensity peak centered on and around, 268nm, 300nm and 320 nmfor NaCdOx and CdOx crystals were attributed to n-π^* transition within oxygen-metal (O-M) group and took an intense red emission. In addition to that, the sharp absorption peaks observed in the UV region were due to the absorption of UV light by the Cd^{2+} ions resulting in the splitting of transition to energy levels from the highest occupied orbital to the lowest unoccupied orbital.

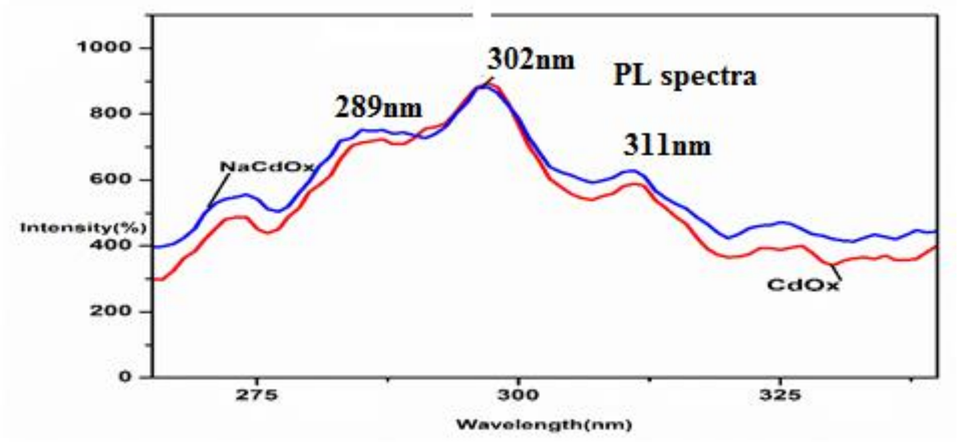

Figure.8.PL spectrum of CdOx and NaCdOx crystals

The amount of splitting of the high intensity energy levels in NaCdOx was high compared to the CdOx crystal stands due to the diffusion of $sodium^+$ ions into the ligand about Cd^{2+} metal ion.

3.6. Dielectric Studies.

The results of the dielectric constant (ε_r) and AC conductivity for CdOx and NaCdOx crystals were calculated for various frequencies by using the equations (5) and (6),

$$\varepsilon_r = Cd/\varepsilon 0A\ . \qquad (5)$$

and

$$\sigma_{ac} = \omega\varepsilon_0\varepsilon_r\tan\delta. \qquad (6)$$

where 'ε_0' is the vacuum dielectric constant (8.85×10^{-12} / farad/m), 'ε_r' is the relative dielectric constant and 'ω' is the angular frequency ($\omega = 2\pi f$) of the applied field.

The value of Dielectric constant ($\varepsilon r_)$ at 1 MHz for CdOx and NaCdOx was 80.25 and 81.5 was shown in **Fig.9 (a).**

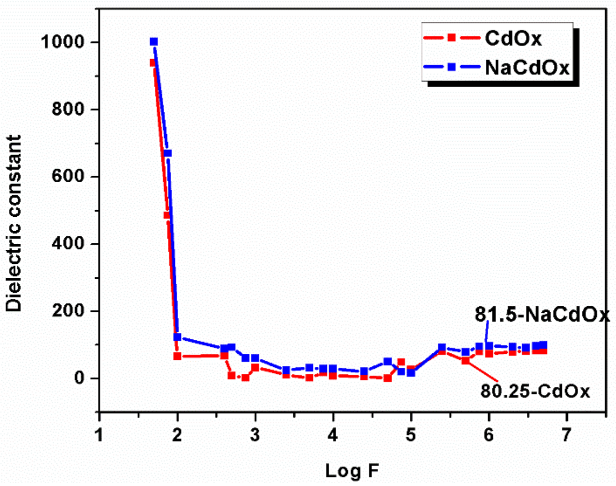

Figure.9 (a).

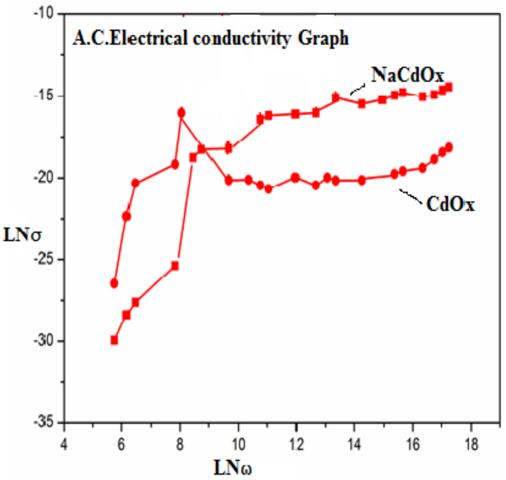

Figure.9 (b).

Figure. 9 (a). Graphical plot of dielectric constant ε_r Vs. Frequency Log f for NaCdOx and CdOx crystals.
Figure. 9 (b). Graphical plot of Electrical conductivity Lnσ vs. Angular frequency Lnω for Na CdOx and CdOx crystals

The high value of dielectric constant ($\varepsilon_{r)}$ at low frequency and to the presence of all polarizations and its low value at higher frequencies may be due to the significant loss of all polarizations gradually.Space charged polarization was generally active at lower frequencies and high temperatures, which showed the perfection of the crystal under study [**32, 33**].

The AC conductivity measurements (σ_{ac}) are calculated for the CdOx and NaCdOx crystals were shown in **Fig.9 (b).** The variation on AC conductivity with various angular frequencies of the CdOx and NaCdOx crystals represented that the value of AC conductivity increases to increase in the frequency. As seen from the plot of Lnσ vs Lnω of NaCdOx was slightly higher compared to the CdOx crystals resulting in the electronic exchange of the number of ions in the NaCdOx crystal, stretched more local displacement of electrons in the direction of the applied field than the CdOx, which in turn contributed rise to polarization. The dielectric behavior of the as-grown crystals revealed that the material required low loss.

IV. CONCLUSIONS

Single crystals of NaCdOx and CdOx have been obtained by single diffusion silica gel method. The crystal growth observations were revealed the dependence of morphology and the ultimate size of crystals on growth parameters like gel concentration, gel age, gel pH and the concentration of upper and lower reactants. The results of the structural analysis were indicating that the complex formed by Na-O and Cd-O coordination bonds were a two-dimensional network structure which was further linked by O-H···O hydrogen bonds to give a three-dimensional structure. On adding Sodium, the triclinic structure of CdOx transformed into a monoclinic structure was confirmed by SXRD diffraction studies. FTIR band assignments were confirmed the presence of water of crystallization, expected metal-oxygen bonded groups and all the vibrational modes of the as-grown cadmium (II) metal complexes. The DSC analysis revealed the gel-grown cadmium oxalate and the sodium cadmium oxalate crystals of the dehydration and decomposition temperatures of NaCdOx crystal was superior to the CdOx crystal confirmed the influence of Na^+ ion in the cadmium oxalate structure matrix. The 98.4% of the optical transmittance and the band gap energy together with moderate refractive index and the significant ionic conductivity of the NaCdOx crystal was found to be higher than the CdOx crystal was studied from the UV, PL and dielectric studies and confirmed that the grown crystal NaCdOx could be a suitable material for the fabrication of opto-electronic devices.

V .ACKNOWLEDGEMENTS

The authors are also thankful to University Grants Commission, Grant no.F.NO: MRP-5808/15 (SERO/UGC) for providing financial support under Minor Research Project (MRP) scheme. We extend our heartfelt thanks to the Director, Central Electro Chemical Research Institute (CECRI), Karaikudi for UV, PL&DSC studies, Mr. Vincent, St. Joseph's college, Bishop Gaspar Central Instrumentation Facilities, Tiruchirappalli for FT-IR studies and also Dr. Sudha Devi, Sophisticated Analytical Instrument Facilities (SAIF), IIT-Chennai, for single crystal XRD analysis.

REFERENCES

[1]. G. Vanhoyland, F. Bouree, M.K. Van Bael, J. Mullens, L.C. an Poucke. Structural determination of refinement of acid strontium oxalate from X- ray and neutron powder diffraction, J. Solid State Chem.157, 2001, 283-288.

[2]. Daniel J. Price, Annie K. Powell, Paul T. Wood. Hydrothermal crystallization and X-ray structure of anhydrous strontium oxalate, *Polyhedron, 18,* 1999, 2499-2503.

[3]. M. E. Torres, T. Lopez, J. Peraza, J. Stockel, and A. C. Yanes. Structural and dielectric characterization of cadmium tartrate,*Journal of Applied Physics, 84,* 1998,5729-5732.

[4]. M.E.Torres, A.C.Yanes, T.Lopez, J.Stockel, J.F.Peraza, Characterization and thermal and electromagnetic behavior of gadolinium-doped calcium tartrate crystals grown by the solution technique, *Journal of Crystal Growth., 156,1*995,156: 421-425.

[5]. T. Thomas et al., Requirements for a GaAsBi 1 eV sub-cell in a GaAs-based multi-junction solar cell,*Semicond. Sci. Technol,30,*2015, 094010 (6pp).

[6]. P.Schuster, *the hydrogen bond—recent development in theory and experiment*(North-Holland publishing company, Amsterdam, 89, 1977, 348–349).

[7]. M. Narsimhulu, B.Rajub, A.Saritha, D.Narayana Rao, K. A. Hussain. A new room-temperature ultra violet emission material: $K_2 [Ni (C_2O_4)_2(H_2O)_2] 4H_2O$, *Physica B, 472*, 2015, 45–48.

[8]. M. Packiya raja, S.M. Ravi Kumarb, R. Srineevasan, R. Ravisankar, Synthesis, growth, and structural, optical, mechanical, electrical properties of a new inorganic nonlinear optical crystal: Sodium manganese tetrachloride (SMTC), *Journal of Taibah University for Science. 11*, 2017, 76–84L.

[9]. Zhao, G. F. Xu, and J. Tang, Carboxylato - bridged 3D polymeric networks of Pr (III): synthesis, crystal structure, magnetic property and thermal behavior,*Journal of Molecular Structure.979,*2010, 160–164.

[10]. C. Wang, G. Guo, and P. Wang, Two sodium and lanthanide (III) MOFs based on oxalate and V-shaped 4, 4'-oxybis (benzoate) ligands: hydrothermal synthesis, crystal structure, and luminescence properties,*Journal of Molecular Structure. 1032*, 2013, 93–99.

[11]. Z. Jin, H. Zhao, D. Yang, X. Yao, and G. Zhu, A novel 3D porous cadmium(II) MOF based on conjugated ligand with potential application for sensing small linear conjugated molecule,*Inorganic Chemistry Communications. 25,*2012, 74 – 78.

[12]. Jagannathan, N. and Mohan Rao, P. Studies on Impurity Incorporation in Cadmium Oxalate Crystals Grown by Gel Method, *Bulletin of Materials Science. 16*, 1993, 16: 365 - 370.

[13]. C. Amuthambigai, C. K. Mahadevan, X. Sahaya Shajan. Growth and characterization of bimetallic (Na and K) phthalate single crystals, *Appl. Phys. A, 122*, 2016, 901 - 908.

[14]. R.Vaidhyanathan, Srinivasan Natarajan, and C. N. R. Rao. Open-Framework Cadmium Oxalates with Channels Stabilized by Alkali Metal Ions,*Journal of Solid State Chemistry. 162*, 2001, 150-157.

[15]. B B Parekh, P.M Vyas, Sonal R Vasant and M J Joshi. Thermal, FT-IR and dielectric studies of gel grown sodium oxalate single crystals, *Bull. Mater. Sci. 31*, 2008, 143–147

[16]. Shedam, M.R. and Venkateswara Rao, A. Effect of temperature on nucleation and growth of cadmium oxalate single crystals in silica gels,*Materials Chemistry and Physics.52*, 1998, 263-266.

[17]. Raj, A.M.E. Optimized Growth and Characterization of Cadmium Oxalate Single Crystals in Silica Gel. *Solid State Sciences, 10,* 2008, 557 – 562.

[18]. S.H. Rahaman, R. Ghosh, T.H. Lu, B.K. Ghosh, Chelating N,N′ - (bis (pyridin-2-yl) alkylidene) propane-1,3-diamine pseudohalide copper(II) and cadmium(II) coordination compounds: Synthesis, structure and luminescence properties of $[M(bpap)(X)]ClO_4$ and $[M(bpap)(X)_2]$ [M = Cu, Cd; X=N3-, NCS^-],*Polyhedron, 24*, 2005, 1525-1532.

[19]. Rui-Qin Zhong et al, A novel 3D micro porous metal-organic framework of cadmium (II) oxalate with diamondoid network,*Inorganic Chemistry Communications,11,*2008, 951–953.

[20]. Brown less N. J., Edwards D. A. and Mohan M. F. Some complexes derived from zinc salicylate or 3, 5-di-tert-butylsalicylate. The crystal structure of (2, 2′-bipyridyl) (methanol) (O-salicylato) (O, O′-salicylato) zinc, *Inorg. Chim. Acta, 287*, 1999, 89-94.

[21]. 15. Kokkonen P., Lajunen L.H.J., Jaakkola A. and Ruotssalainen, Kinetic and mechanistic studies on the decomposition of some hydrous iron (II) salicylato complexes, *Thermochim. Acta, 79*, 1984, 289-298.

[22]. R.L. Frost, Raman spectroscopy of natural oxalates, *Anal. Chim. Acta, 517*, 2004, 207-214.

[23]. R.L. Frost, M.L. Weier, Raman spectroscopy of natural oxalates at 298 and 77 K, *J. Raman Spectrosc, 34*, 2003, 776-785.

[24]. G.M. Begun, W.H. Fletcher, Vibrational spectra of aqueous oxalate ion, *Spectrochim. Acta, 19*, 1963, 1343-1349.

[25]. Christensen, A. N., Lebech, B., Andersen, N. H., &Grivel, J-C, The crystal structure of paramagnetic copper (ii) oxalate (CuC2O4): formation and thermal decomposition of randomly stacked anisotropic nano-sized crystallites. *Dalton Transactions, 43(44),* 2014, 16754-16768.

[26]. K. Ambujam, K. Rajarajan, S. Selvakumar, I. VethaPotheher, Ginson P. Joseph, P. Sagayaraj, Growth and characterization of a novel NLO crystal bis-glycine hydrogen chloride, *J.Cryst. Growth. 286*, 2006, 440-444.

[27]. Anthoni Praveen Menezes, A. Jayarama, SeikWeng N, Synthesis, crystal growth and characterization of a D-π-A type novel organic nonlinear optical single crystal, *J. Cryst. Growth, 402*, 2014, 130-137.

[28]. A.Ashour, N. EI-Kadry, S.A. Mahmoud, on the electrical and optical properties of CdS films thermally deposited by a modified source, *Thin Solid Films, 269*, 1995, 117-120.

[29]. T.S.Moss, Relations between the Refractive Index and Energy Gap of Semiconductors, *J.Phys.Stat.Sol (B), 131*, 1985, 415-427.

[30]. C. RamachandraRajaa, G. Gokilab, A. Antony Joseph, Growth and spectroscopic characterization of a new organic nonlinear optical crystal: l-Alaniniumsuccinate, *spectrochimicaActa Part A. 72*, 2009, 753–756.

[31]. Tauc J, Grigorovici R. Vancu, Optical Properties and Electronic Structure of Amorphous Germanium, *Physica Status Solidi B, 15*, 1966, 627-637.

[32]. K.K Bamzai, S. Suri, V. Singh, Synthesis, characterization, thermal and dielectric properties of pure and cadmium doped calcium hydrogen phosphate, *Mater Chem Phys, 135*, 2012, 158 –67.

[33]. S. Parthiban, S. Murali, G. Madhurambal, S.P.Meenakshisundaram, S.C.Mojumdar, Effect of zinc (II) doping on thermal and optical properties of potassium hydrogen phthalate (KHP) crystals, *Therm Anal Calorim, 100,*2010, 751–756.

IOSR Journal of Engineering (IOSRJEN) is UGC approved Journal with Sl. No. 3240, Journal no. 48995.

F. Daisy Selasteen"A Study on the Synthesis, Structural, Spectral and Optoelectronic Properties of Pure and Sodium Ion Incorporated Cadmium Oxalate Nonlinear Optical Single Crystals” IOSR Journal of Engineering (IOSRJEN), vol. 08, no. 9, 2018, pp. 52-61.