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ChemTech

International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.4, No.2, pp 739-748, April-June 2012

Spectral, Thermal, Dielectric Studies and Crystal Structure of Novel Nonlinear Optical Diaquabis(Salicylato)Zinc

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Abstract: Single crystals of salicylato complex of zinc with high degree of transparency were grown from aqueous solution by slow evaporation technique. The stoichiometric composition of the crystals is established by CHN analysis. Single crystal X- ray diffraction analysis reveals that the crystal belongs to monoclinic system with space group C_2. The FTIR spectra of the grown crystals were recorded and analyzed. The thermo gravimetric (TG) and differential thermal analyses (DTA) were carried out to understand the thermal stability of the sample. The kinetic and thermodynamic parameters were also calculated. The compound showed nonlinear optical property with Kurtz powder second harmonic generation test. Optical behaviour of the crystal was investigated using UV –Vis spectroscopy. The optical absorption study reveals the transparency of the crystal in the entire visible region. The optical band gap is found to be 4eV. The dielectric constants of the sample were also studied.

Keywords: Crystal growth from solution; Crystal structure; Nonlinear optical study; Dielectric property.

1. INTRODUCTION

Non linear optics (NLO) is a frontier field in science and technology, which has found wide applications in the field of telecommunication, optical information, optical storage devices, frequency conversion for lasers etc. [1,2]. Now-a-days organic crystals are highly recognized as materials of the future because of high nonlinearities and rapid response to electro optic effect, as compared to inorganic NLO materials. Their molecular nature, combined with versatility of synthetic chemistry can be used to alter the structure in order to maximize the nonlinear properties [3,4]. Organic NLO materials play a vital role in second harmonic generation (SHG), frequency mixing, electro-optic modulation, optical parametric oscillation, optical bi-stability, optical image processing, colour displays, underwater communications and medical diagnostics etc.[5]. Organic nonlinear materials have the advantage that they are less costly and can be synthesized fairly easily. In the last decade, organic nonlinear optical crystals with aromatic rings have attracted much attention because of their high nonlinearity, fast response and tailor made flexibility. From a coordination standpoint, salicylic acid is a versatile ligand with benzene ring, displaying a variety of bonding modes. The salicylate ion $C_7H_5O_3^-$ contains both the carboxylic and hydroxyl functional groups and with this ion represents a bonding typical of the more complicated natural materials. Some metal salicylato complexes have been used as additives in medicine. Zinc which is one of the most abundant trace elements in the body is an important component of many proteins. Zinc carboxylates with organic ligands are interesting because of their potential biological activity. A zinc complex based on salicylic acid derivatives (E-84 from Orient Chem.) is a powerful charge-control agent for toners used in electro photography. Many of the zinc complexes are luminescent materials with potential applications in opto-electronic devices [6]. The luminescent property of Tb^{3+} doped zinc salicylates and the relationship between the luminescent property and crystal structures have been reported earlier [7]. In this paper we report the nonlinear property of the title compound which has not been reported so far.

Crystal growth from solution is a very important process that is used in many applications from the laboratory to the industrial scale. In the present paper, the single crystals were grown by slow evaporation technique and characterization studies such as single crystal XRD, FTIR, UV – VIS and TG- DTA have been carried out. The NLO and dielectric properties of the single crystal have also been studied.

2. EXPERIMENTAL PROCEDURE

All the reagents used in this experiment were of analytical grade procured from CDH. An aqueous solution (100ml) of sodium hydroxide of molarity 2M was prepared. Salicylic acid (27.5g) was added to this solution and stirred well so that an aqueous solution of sodium salicylate was obtained. Zinc chloride (13.54g) was dissolved in 100ml of distilled water, filtered and to this solution, sodium salicylate was added drop wise with stirring to get a white precipitate. This precipitate was filtered and dissolved in required quantity of distilled water to get a saturated solution. This solution was kept at room temperature to grow crystals.

3. RESULTS AND DISCUSSION

3.1. GROWTH CHARACTERISTICS

Tiny crystals were found to grow in the solution after three weeks. The size of the crystal gradually increased to 4mm x 3mm x 2mm after two months. The crystals are found to be transparent and rectangular in shape. The characteristic habit of the crystals is shown in figure 1.

3.2. SINGLE CRYSTAL X-RAY DIFFRACTION STUDIES

A well formed single crystal was subjected to SXRD studies using Bruker Kappa Apex II X-ray spectrometer to estimate the lattice parameters. The crystallographic data and processing parameters are given in table 1. Anisotropic displacement parameters were applied to non hydrogen atoms in full matrix least square refinement based on F^2. The hydrogen atoms were assigned common isotropic displacement factors and are included in the refinement cycles by the use of geometrical restraints. The programs APEX 2 /SAINT, SAINT/XPERP, SHELXL-97, and SIR 92 were used for computation. The IUCR software MERCURY is used for molecular graphics. Fractional atomic coordinates are listed in table 2.

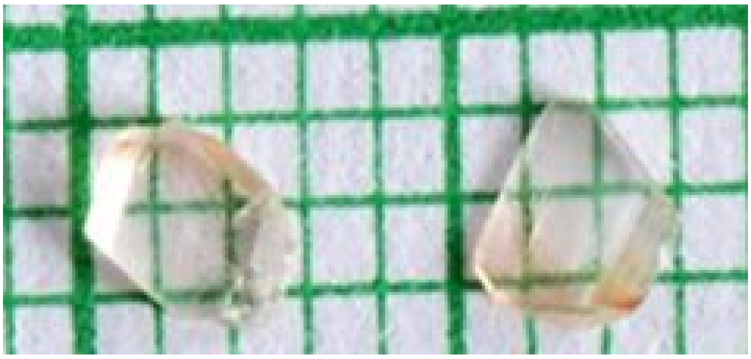

Fig.1 Single crystals of C_{14} H_{14} O_8 Zn.

Table 1: Crystal Data and Structure Refinement Parameters

Formula	$C_{14}H_{14}O_8Zn$
CCDC deposit no.	814410
Colour	colourless
Chemical formula weight	375.62
Temperature (K)	293(2) K
Wavelength (Å)	0.71073
Crystal system	Monoclinic, C2
Unit cell dimensions (Å)	a = 15.4674(17) Å, b= 5.3431(6) Å c = 9.1715(10) Å, β = 93.524(3) deg
Volume , Z	756.53(14) Å^3, 2
Calculated density	1.649 mg/m^3
Absorption coefficient	1.663 mm^{-1}
F(000)	384
Crystal size	0.30 x 0.20 x 0.20 mm
Theta range for data collection	2.22 to 31.85 deg.
Index ranges	-22<=h<=22, -3<=k<=7, -13<=l<=13
Reflections collected	5386
Independent reflections	1895 [R(int) = 0.0266]
Completeness to theta = 28.29	97.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.781 and 0.652
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1895 / 4 / 113
Goodness -of -fit on F^2	1.130
Final R indices[I>2sigma(I)]	R1 = 0.0289, wR2 = 0.0682
R indices (all data)	R1 = 0.0368, wR2 = 0.0733
Largest diff. peak and hole	0.587 and -0.402 e.A^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for single crystal of $C_{14}H_{14}O_8Zn$.U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

Atom	x	y	z	U(eq)
C(1)	6242(1)	3200(9)	7525(2)	31(1)
C(2)	5900(2)	1494(6)	6504(3)	45(1)
C(3)	6415(2)	-259(7)	5889(3)	53(1)
C(4)	7299(2)	-335(6)	6312(3)	51(1)
C(5)	7652(2)	1343(6)	7307(3)	44(1)
C(6)	7135(1)	3145(9)	7913(2)	32(1)
C(7)	5666(1)	5015(5)	8210(2)	34(1)
O(1)	4244(1)	10617(4)	8878(3)	59(1)
O(2)	4863(1)	4922(4)	7995(2)	49(1)
O(3)	6004(1)	6635(4)	9093(2)	42(1)
O(4)	7512(1)	4753(4)	8900(2)	47(1)
Zn(1)	5000	8219(1)	10000	38(1)

Co-ordination environment of the complex with atom numbering scheme is shown in figure 2. In the present structure Zn(1) is coordinated with six oxygen atoms: four from two chelating salicylate groups and two from two water molecules. In the reported structure of zinc salicylate dihydrate oxygen coordination about the zinc is tetrahedral [8]. The Zn-O distances of coordinated salicylate oxygen atoms are, Zn(1)-O(2) = 2.546(2) Å and Zn(1)-O(3) = 1.9942(2) Å and for aqua oxygen, Zn(1)-O(1) = 1.9805(2) Å. This shows that the chelating salicylate ligand is bonding in an asymmetric manner. The bond distances Zn(1)-O(1) and Zn(1)-O(3) are found to be almost similar to other reported zinc complexes coordinated to salicylate ligand [9]. But in the present structure Zn(1)-O(2) shows significant variation. The bond angles around Zn atom are shown in table 3. The bond angle of O(2)-Zn(1)-O(3) is 55.78° whereas the average acute angle formed by bidentate salicylate ligand at Zn site of $[\mathrm{Zn_{2\text{-}}(Hsal)_4(4,4'\text{-}bpe)_2}]$ is 57.55° and that of $[\mathrm{Zn(salH)_2(bipy)(MeOH)}]$ is 59.2° [10,11]. The packing of the crystal viewed along the b- axis is shown in figure 3. The shortest Zn-Zn distances along a, b and c axes are 8.182, 5.343, 9.172 Å respectively, indicating the absence of direct metal-metal interaction.

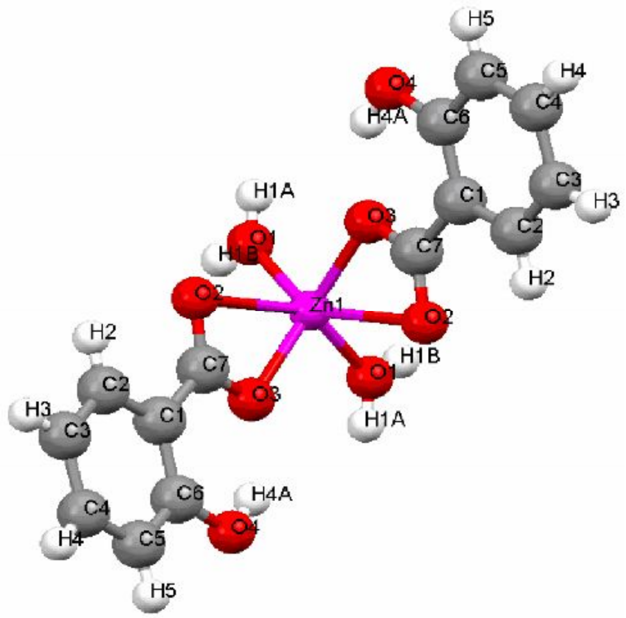

Fig 2. Molecular structure of $C_{14}H_{14}O_8Zn$ with atom numbering.

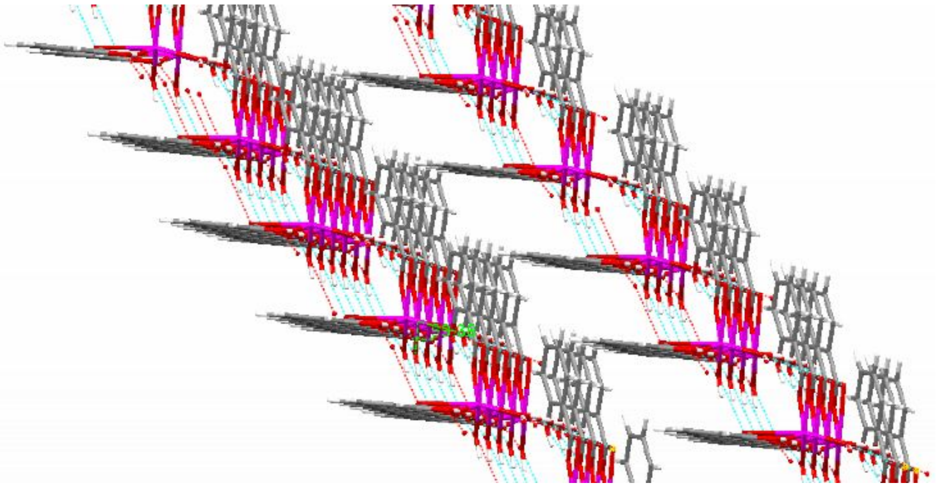

Fig 3.View of the packing along the crystallographic b axis of the $C_{14}H_{14}O_8Zn$ crystal

Table 3. Selected bond lengths (Å), bond angles and torsion angles (°) for the Complex

Zn(1) - O(1)	1.9805(19)	Zn(1) - O(3)	1.9942(17)
Zn(1) - O(2)	2.546	C(7)-O(3)	1.276(3)
C(7)-O(2)	1.246(3)	-	-
O(2)-Zn(1)-O(3)	55.78	O(2)-C(7)-O(3)	119.6(2)
O(1)-Zn(1)-O(3)	120.53(9)	C(7)-O(3)-Zn(1)	104.66(13)
O(3)-C(7)-C(1)	118.61(19)	C(2)-C(1)-C(7)	120.07(18)
C(2)-C(1)-C(6)	119.0(3)	C(3)-C(2)-C(1)	121.3(2)
C(6)-C(1)-C(7)	120.9(3)	C(5)-C(4)-C(3)	120.6(2)
C(2)-C(3)-C(4)	119.2(2)	O(4)-C(6)-C(5)	118.19(17)
C(4)-C(5)-C(6)	120.3(2)	C(5)-C(6)-C(1)	119.6(3)
O(4)-C(6)-C(1)	122.2(3)	O(2)-C(7)-C(1)	121.7(2)
O(2)-C(7)-O(3)	119.6(2)		

Each molecule is linked to a neighbor unit via hydrogen bonding interactions through the coordinated water molecule and the oxygen of salicylate (table 4). The characteristic intramolecular hydrogen bond of salicylic acid is also seen in the present crystal and this leads to the generation of six-membered ring system involving O(3), C(7), C 1), C(6), O(4), H(4A), O(3).

3.3. ELEMENTAL ANALYSIS

The chemical composition of the synthesized material was determined by carbon, hydrogen and nitrogen (CHN) analysis using Elementar Vario ELIII CHN Analyser.

Result obtained from CHN analysis is compared with the theoretical value of carbon, hydrogen and nitrogen present in diaquabis(salicylato)zinc and is given in table 5. It is observed from the result that the composition of the synthesized material is $C_{14}H_{14}O_8Zn$.

3.4. FOURIER TRANSFORM INFRARED (FTIR) SPECTRA

The infrared spectrum of the sample was recorded in KBr phase in the frequency region 4000 – 400 cm^{-1} using Thermo Nicolet, Avatar 370 model spectrometer. Figure 4 shows the IR spectrum recorded in the range 500-4000 cm^{-1}. The broad band around 3200 cm^{-1} can be attributed to the stretching absorptions of the OH groups originating from water molecules [11,12]. The asymmetric stretching vibration bands of carboxylate groups emerging at 1623 and 1596 cm^{-1} suggest the presence of two coordination modes [13] and the band at 1487 and 1466 cm^{-1} are assigned to symmetric stretching of COO^- group of the complex [14]. The $\Delta\upsilon$ ie., the separation between υ_{asy} and υ_{sy}, is 133cm^{-1} which indicates chelate bidentate coordination of carboxylate group to the central metal ion as is evident from single crystal x-ray diffraction studies. In the ligand, the corresponding υ_{asy} and υ_{sy} bands are at 1657, 1612, and 1483, 1443 cm^{-1} respectively. This shift of carboxyl stretching vibration strongly supports its coordination to Zn ion [10]. The IR band at 1340 cm^{-1} corresponds to the C-OH bending of the phenol group and the band at 1239 cm^{-1} is due to the stretching of the phenol group. The band at 1152 cm^{-1} is due to the bending in the C-H-C plane in the substituted aromatic ring. The band at 876 cm^{-1} corresponds to scissoring vibrations in the carboxyl groups. The peak at 761cm^{-1} corresponds to out of plane bending of hydrogen atoms in the benzene rings. The band at 570 cm^{-1} corresponds to Zn-O bond [15, 16].

Table 4. Hydrogen bonds for the complex

D-H---A	d(D-H)	d(H---A)	d(D---A)	<(DHA)
O(4)-H(4A)...O(3)(intra molecular)	0.82	1.83	2.557(2)	146.8
O(1)-H(1B)...O(2)#2	0.845(10)	1.837(16)	2.638(3)	158(3)
O(1)-H(1A)...O(4)#3	0.834(10)	1.905(14)	2.718(2)	165(5)

Table. 5 Percentage compositions of C and H as obtained by CHN analysis

Element	Composition	
	Theoretical	Measured
Carbon	44.76	44.9
Hydrogen	3.75	3.7

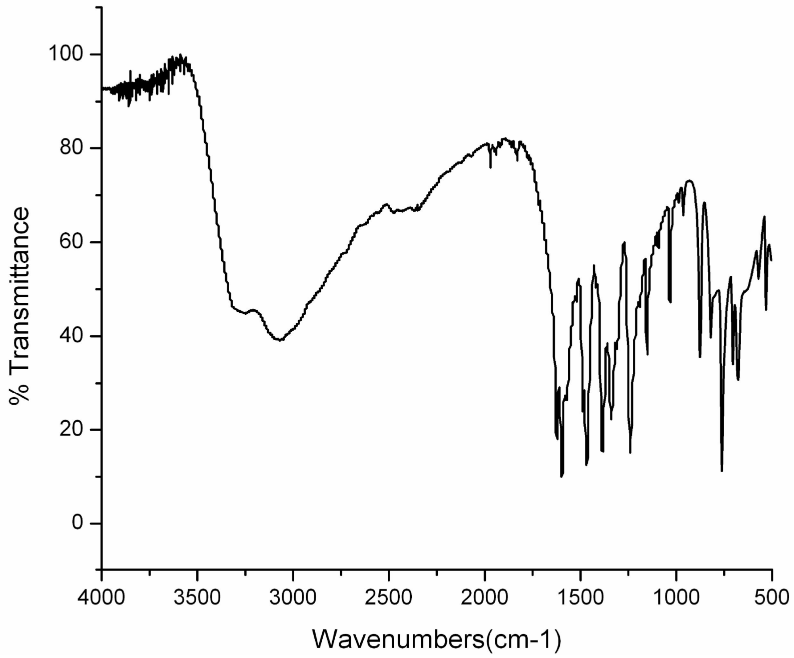

Fig.4 FT- IR spectrum of the grown crystals

3.5. THERMAL STUDY

Thermal properties of the grown crystals were studied using Perkin Elmer Diamond TG/DTA analyzer with a heating rate of 10°C/min in the nitrogen atmosphere. The results obtained from TGA and DTA studies are shown in figure 5. The compound is thermally stable upto 100°C. Above this temperature the compound starts to decompose with the release of two water molecules in the temperature range 100 - 140°C (experimental mass loss 10.47%, theoretical mass loss 9.607%). The dehydration of the complex is indicated by endothermic peaks at 107.93°C on the DTA curve. Next step of the thermal decomposition in the temperature range 200 - 300°C is the release of one salicylic acid molecule and formation of Zn (OC_6H_4COO) [17]. This corresponds to an endothermic peak 252.47°C on the DTA curve (experimental mass loss 36.29%, theoretical mass loss 36.77%). The third step in the temperature range 350 - 460°C corresponds to the release of the second salicylato ligand resulting in the formation of ZnO. The remaining weight of 17.95 % corresponds to the final product ie, ZnO [15,16]. The first two stages are endothermic while the third stage is a strong exothermic process [18].

The Coats and Redfern method has been used to determine the kinetic parameters of decomposition ie, order of reaction, activation energy (E), and pre-exponential term logA [19]. The other thermodynamic parameters such as the standard enthalpy and standard Gibb's free energy (ΔG) were also calculated [20]. The calculated values of kinetic parameters are given in table 6.

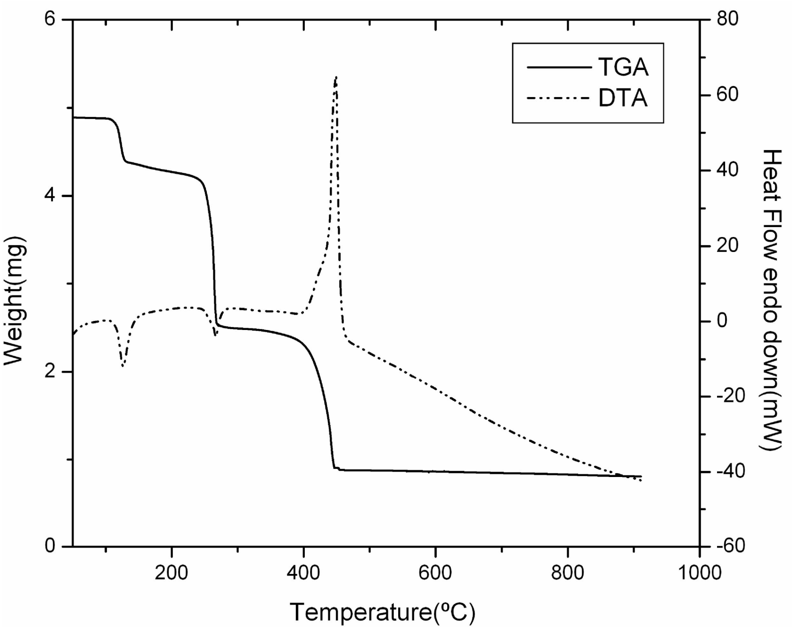

Fig.5 TG/DTA curves of $C_{14}H_{14}O_8Zn$

Table.6 Kinetic and thermodynamic parameters of dehydration (stage I) and decomposition (stage II and stage III) of $C_{14}H_{14}O_8Zn$

Kinetic parameters				Thermodynamic parameters		
stage	n	E KJ/mol	logA S^{-1}	S J/Kmol	ΔH KJ/mol	ΔG KJ/mol
I	1.1	275.97	34.84	420.019	269.63	109.63
II	0.9	193.41	16.798	71.94	184.67	146.87
III	0.9	217.70	13.96	14.95	-205.707	194.92

3.6. UV – VISIBLE –NIR SPECTROSCOPY

The UV-Vis-NIR spectrum of $C_{14}H_{14}O_8Zn$ was taken in the wavelength range between 200 and 2000 nm using the instrument Varian Cary 5000. The UV–Vis–NIR spectrum of $C_{14}H_{14}O_8Zn$ is shown in figure 6. It is seen from the spectra that absorption is not observed in the entire visible region. In the entire region (200-2000nm), the crystal is optically transparent. The maximum absorption lies around 350nm. Even in this region the crystal is optically transparent with more than 75% transmission level. This transparent nature is essential for NLO applications. A graph is drawn between photon energy (hυ) verses (α hυ) where α is the absorption coefficient and the band gap is estimated as 4eV by extrapolating the linear portion of the curve to zero absorption fig. 7. From the value of Eg one can calculate the polarizability and the calculated value agrees well with Clausius Mossotti relation.

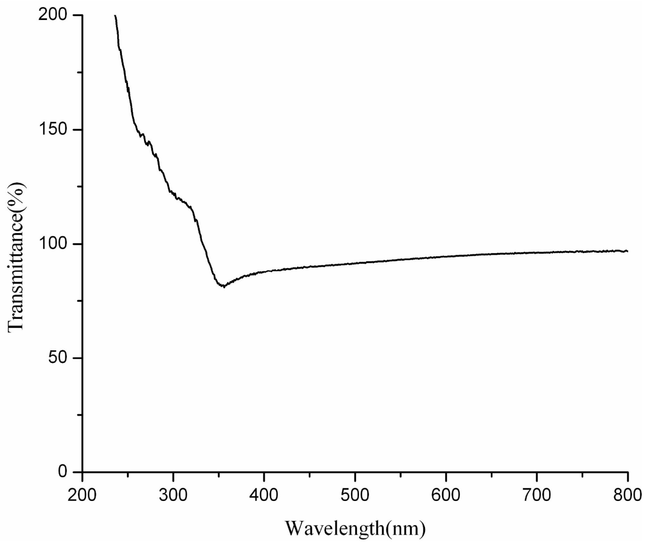

Fig.6 UV-Vis spectrum of the grown crystal

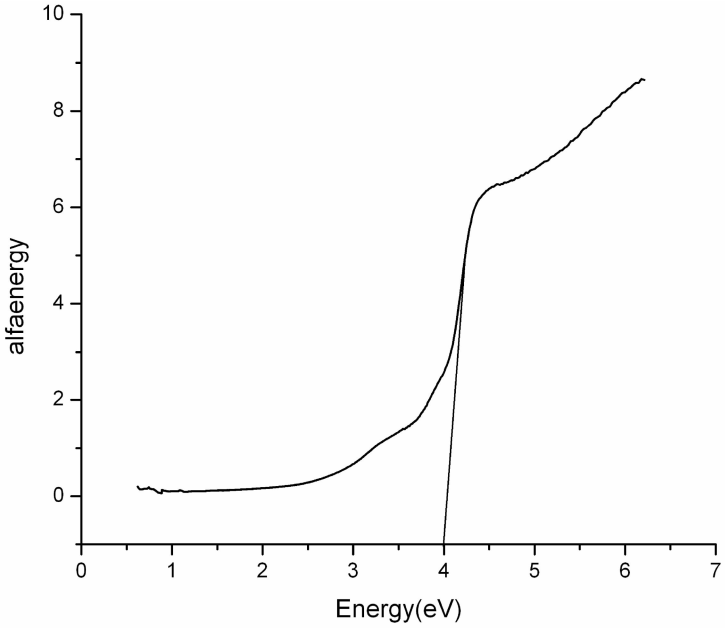

Fig.7 Plot of αhυ versus photon energy

3.7. NON – LINEAR OPTICAL STUDIES

Kurtz and Perry powder second harmonic generation (SHG) method was used to predict the NLO behaviour of the crystal. The sample was tested using high intensity Nd – YAG laser (λ = 1064 nm). Kurtz powder SHG experiments have been carried out for diaquabis(salicylato)zinc . The input power of the laser beam was measured to be 4.0 mj/pulse. The emission of green radiation from the sample ascertains the SHG property of the grown crystal. A second harmonic signal of 130mV/pulse was obtained, while the standard KDP crystal gave a SHG signal of 11mV/pulse for the same input energy.

3.8. DIELECTRIC STUDIES

The dielectric constant of the crystal was studied in the frequency region 500Hz – 4MHz using LCR meter (Hioki 3532-50, LCR Hitester, Nagano, Japan). The specimen was used in the form of compressed pellets of diameter 11 mm and thickness 2mm prepared from the fine powder of the crystals. The pellet was coated with silver paste on both surfaces to ensure good electrical contact and placed between two copper electrodes to form a parallel plate capacitor.

The variation of dielectric constant of the grown crystal as a function of frequency is shown in figure 8. From the graph, the dielectric constant is seen to decrease with increase in frequency. The large value of dielectric constant at low frequency is due to the presence of space charge polarization [21]. The decrease in the value of dielectric constant with frequency is due to the fact that the frequency of electric charge carriers cannot follow the alternation of the ac electric field applied beyond a certain critical frequency [22]. The very low value of dielectric constant at higher frequencies is important for the fabrication of materials for ferroelectric, photonic and electro-optic devices. The value of dielectric constant at higher frequencies can be used to calculate Penn gap, Fermi energy and polarisability of the grown crystals [23]. The calculated values are depicted in table 7.

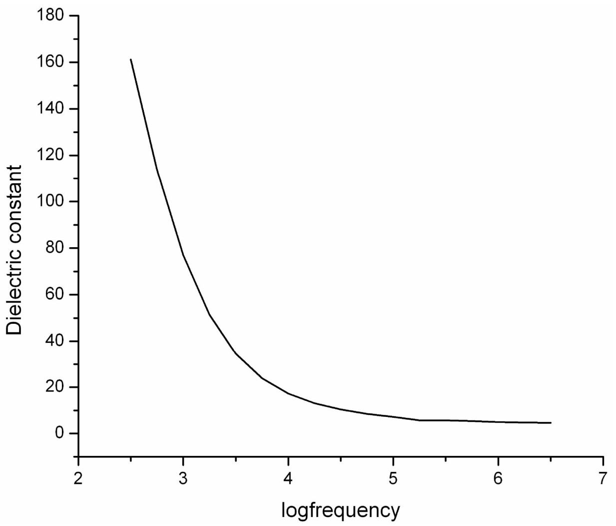

Fig.8 Frequency dependence of dielectric constant of the grown crystal.

Table 7. Plasma energy and polarisability of $C_{14}H_{14}O_8Zn$ crystal.

Parameters	Values
Plasma energy (eV)	20.90
Penn gap (eV)	10.447
Fermi gap (eV)	16.97
Polarizability(cm^3) (a) Penn analysis (b) Clausius-Mossotti Equation (c) from band gap	 4.804×10^{-23} 5.163×10^{-23} 4.576×10^{-23}

3.9 CONCLUSION

Single crystals of Diaquabis(salicylato)zinc have been successfully grown by slow evaporation technique. Single crystal X- ray diffraction study confirms that the grown crystals belong to monoclinic system (C2) with unit cell parameters a=15.4674(17) Å, b=5.3431(6) Å, c=9.1715(10) Å, β=93.524(3). The elemental analysis is consistent with the formula $C_{14}H_{14}O_8Zn$. Kinetic and thermodynamic parameters were calculated from TGA/DTA studies. Fundamental parameters of the grown crystals were calculated from unit cell parameters and dielectric studies. Energy gap is determined from UV–Vis spectroscopy. The value of polarisability determined from UV-Vis-NIR and dielectric studies agrees well with that calculated using Clausius-Mossotti relation. The transparent nature together with high nonlinearity of the crystal is suited for fabrication of photonic devices.

SUPPLEMENTARY DETAILS

CCDC No. 840550 contains the supplementary crystallographic data for the compound $C_{14}H_{14}O_8Zn$. These data can be obtained free of charge via htt://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 IEZ, UK; fax: (+44)1223-336-033; or e-mail: data request @ccdc.cam.ac.uk

ACKNOWLEDGEMENT

One of the authors Bijini. B.R. is grateful to the UGC for awarding teacher fellowship under FIP. The authors also express their gratitude to STIC, Kochi for providing facilities for characterization studies.

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