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RESEARCH ARTICLE

STRUCTURAL, THERMAL, DIELECTRIC AND LDT STUDIES OF NEW NLO MATERIAL: L-HISTIDINIUM 5 SULFOSALICYLATE

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ABSTRACT

L-Histidinium 5 SulfoSalicylate crystal (LH5SS) was grown by a slow evaporation technique at ambient temperature. Solubility of LH5SS in aqueous solution was determined. Single crystal XRD revealed that compound crystallizes in monoclinic crystal system. Thermal stability of the grown crystal was studied by TGA– DTA analysis. The laser damage threshold value of LH5SS crystal was estimated to be 6.78×10^9 GW /cm^2 using a Nd:YAG laser.

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INTRODUCTION

Non-linear optics have got enough importance due to their enormous demand in the recent technologies like lasers, optoelectronics, and data storage systems (Uthra kumar *et al*., 2010; Hanumantha rao and Kalainathan, 2012). Hence the search for new materials exhibiting NLO properties has never ceased in the endeavor to develop new laser sources and extend application in the area of telecommunication and storage. Organic nonlinear materials are attracting a great deal of attention, as they have large optical susceptibilities, inherent ultra fast response times and high optical thresholds for laser power as compared with inorganic materials (Tanusri *et al*., 2003). The salts of amino acids like L-histidine (Saraswathi and Vijayan, 2002), L-lysine (Mahadevan *et al*., 2014), L-arginine (Kalaiselvi *et al*., 2008) are some of the applications which proved their application in the field of NLO. L-Histidine is an important amino acid, which shows higher SHG efficiency like all other amino acids. In the present investigation, an attempt has been made to grow L-Histidinium 5 SulfoSalicylate crystal (LH5SS) by slow evaporation method at room temperature. The grown crystals have been subjected to structural, thermal, dielectric and nonlinear optical studies.

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MATERIALS AND METHODS

Synthesis

L-Histidinium 5 SulfoSalicylate crystal was synthesized from analytical grade L-Histidine and 5 SulfoSalicylic Acid dihydrate. The calculated amount of L- Histidine was dissolved in deionized Millipore water and the equal ratio of 5 SulfoSalicylic Acid dihydrate was added to this by continuous stirring for 4 h. The obtained salt was filtered and dried at room temperature. Single crystals were grown from the saturated solution of LH5SS by slow evaporation technique and the crystals were obtained after repeated recrystallization in 10 days. Good quality crystals were extracted and subjected to various characterization studies.

Solubility

Solubility curve for LH5SS was determined by using double distilled water as a solvent in the temperature range from 35 to 50 ◦C. The solution was maintained at a constant temperature and continuously stirred using an immersible magnetic stirrer to ensure homogeneous temperature and concentration throughout the entire volume of the solution. On reaching saturation, the concentration of the solute was estimated gravimetrically. The variation of solubility with temperature is shown in Fig. 1. LH5SS exhibits a positive solubility–

temperature gradient in aqueous solution, which is very important to grow bulk crystals from solution.

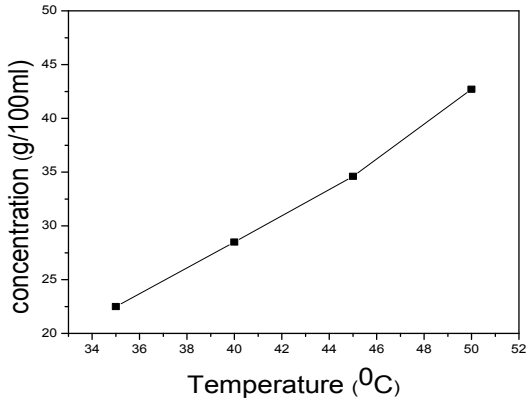

Figure 1. Solubility Curve of LH5SS crystal

RESULTS AND DISCUSSION

Single crystal x-ray diffraction studies

The single crystal diffraction studies were carried out to find the cell parameters and crystal structure of the grown material. The single crystal XRD study reveals that the crystal system belongs to monoclinic system, and the space group is $P2_1$. The crystal data and the structure refinement for LH5SS material is given in Table 1. The structure of the LH5SS crystal has been solved by direct methods and refined by full-matrix least square techniques using SHELXL-2014/7'. The ORTEP diagram of the molecular structure of the grown LH5SS single crystals is shown in Fig. 2. The crystal structure contains L-Histidine and 5Sulfosalicylic acid molecules connected by various hydrogen bonds and the bonds are tabulated in Table 2.

Table 1. Crystal data and structure refinement for LH5SS

Identification code	LH5SS	
Empirical formula	C13 H15 N3 O8 S	
Formula weight	373.34	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 9.5707(17) Å	α= 90°.
	b = 19.038(4) Å	β= 90.711(14)°.
	c = 8.315(2) Å	γ = 90°.
Volume	1514.8(6) $Å^3$	
Z	4	
Density (calculated)	1.637 Mg/m^3	
Absorption coefficient	0.267 mm^{-1}	
F(000)	776	
Crystal size	0.300 x 0.200 x 0.200 mm^3	
Theta range for data collection	2.128 to 24.999°.	
Index ranges	-11<=h<=11, -22<=k<=22, -9<=l<=9	
Reflections collected	23057	
Independent reflections	23057	
Completeness to theta = 24.999°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.92 and 0.89	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	23057 / 13 / 457	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0864, wR2 = 0.2023	
R indices (all data)	R1 = 0.1445, wR2 = 0.2479	
Absolute structure parameter	0.03(10)	
Extinction coefficient	0.015(4)	
Largest diff. peak and hole	0.795 and -0.748 $e.Å^{-3}$	

Table 2. Hydrogen bonds for LH5SS (Å and °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(9)-H(9)...O(1)#1	0.98	2.26	3.21(3)	161.2
C(9)-H(9)...O(10)#1	0.98	2.57	3.14(3)	117.6
C(12)-H(12)...O(1)#1	0.93	2.26	3.04(3)	141.1
C(12)-H(12)...O(10)#1	0.93	2.58	3.25(4)	129.8
C(13)-H(13)...O(6)#2	0.93	2.59	3.10(4)	115.1
C(13)-H(13)...O(13)#3	0.93	2.33	3.09(4)	138.1
C(23)-H(23B)...O(9)	0.97	2.13	3.06(4)	161.8
C(26)-H(26)...O(5)#4	0.93	2.42	3.25(3)	149.7
C(26)-H(26)...O(14)#5	0.93	2.54	3.20(4)	128.6
N(1)-H(1A)...O(3)#2	0.89	2.55	3.04(3)	115.6
N(1)-H(1A)...O(5)#5	0.89	2.26	3.07(3)	149.8
N(1)-H(1B)...O(12)	0.89	2.24	3.05(3)	150.8
N(1)-H(1C)...O(10)#1	0.89	2.19	2.82(3)	126.5
N(2)-H(2A)...O(2)#5	0.89	2.02	2.83(3)	149.3
N(2)-H(2B)...O(4)#6	0.89	2.43	3.12(3)	135.0
N(2)-H(2C)...O(11)#5	0.89	2.07	2.90(4)	155.0
N(2)-H(2C)...S(2)#5	0.89	2.90	3.76(3)	163.3
N(3)-H(3)...O(3)#7	0.86	2.00	2.79(3)	152.1
N(3)-H(3)...S(1)#7	0.86	2.88	3.59(2)	141.8
N(4)-H(4)...O(15)#1	0.86	1.88	2.70(3)	158.2
N(6)-H(6A)...O(11)#8	0.86	2.28	3.13(4)	172.1
N(6)-H(6A)...S(2)#8	0.86	3.01	3.75(3)	145.7
N(7)-H(7)...O(7)#1	0.86	2.21	2.84(3)	130.0
O(4)-H(4A)...O(5)	0.82	1.89	2.59(3)	141.5
O(6)-H(6B)...O(14)#9	0.82	1.63	2.419(18)	160.5
O(8)-H(8)...O(16)#10	0.82	1.66	2.46(2)	163.5
O(12)-H(12A)...O(13)	0.82	1.88	2.59(3)	144.1

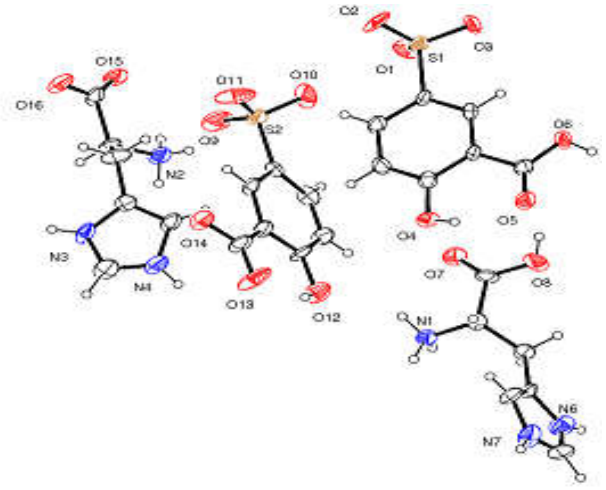

Figure 2. ORTEP diagram of LH5SS crystal

Laser damage threshold studies

The usefulness of NLO crystal depends not only on the NLO property but also greatly on its ability to sustain high intensity laser light (Bhar *et al*., 2000). The pulse width of 6 ns with a repetition rate of 10 Hz and a fundamental wavelength of 1064 nm Gaussian beam was used to measure the laser damage threshold of LH5SS crystal. Laser damage threshold of the crystal was estimated using the relation

$$Power\ density\ P_d = E/\tau A$$

Where A= πr^2, E is the input energy (mJ), τ is the pulse width (ns) and r is the radius of the spot (mm). The calculated values of the LDT of 6.78X10^9 GW/cm^2. Hence, the crystal has a high LDT value. LH5SS crystal can be used for high power frequency conversion applications.

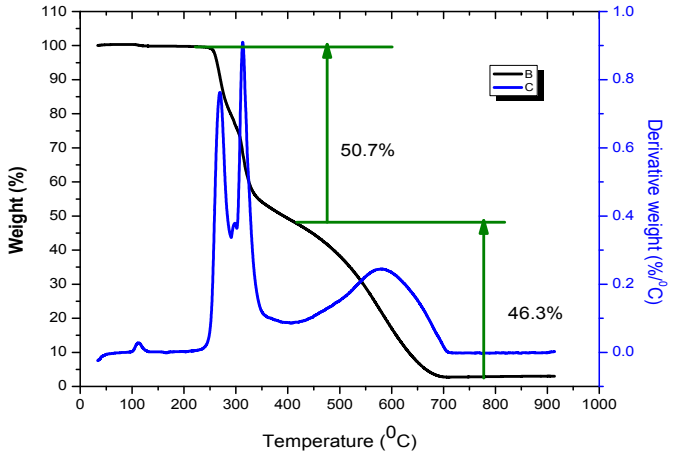

Figure 3. TGA/DTA spectrum of LH5SS crystal

Thermal gravimetric-differential thermal analysis

The thermal analysis of LH5SS was carried out in the temperature ranging from 30 to 900 ˚C at a heating rate of 10˚C/min in nitrogen atmosphere. In TGA, there is no weight loss up to 130 ˚C. This indicates that there is no inclusion of water in the crystal lattice. LH5SS crystal exhibits sharp weight loss starting at 270°C; no weight loss is observed in the thermo gravimetric analysis (TGA) curve below this temperature. It is seen that the major weight loss (around 96%) starts at 270 ◦C and it continues up to 670 ◦C. The nature of weight loss indicates the decomposition point of the material. However, below this temperature, no weight loss has been observed.

Dielectric studies

Single crystal of LH5SS of thickness 1.9 mm was subjected to dielectric studies at 313K, 323K, 333K and 343K for various frequencies ranging from 50 Hz to 5 MHz. It is seen that the value of dielectric constant and dielectric loss decrease exponentially with frequency and increase with temperature. At low frequencies, space charge polarization is more predominant and hence the dielectric constant increases abnormally. The characteristic of low dielectric constant with high frequency of the title compound suggests that the crystal possesses enhanced optical quality with lesser defects and this parameter is most important for nonlinear optical applications (Rao and Smakula, 1965).

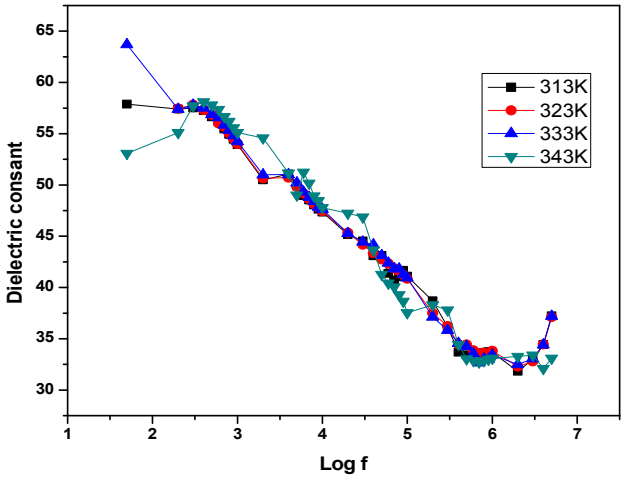

Figure 4. Log f Vs Dielectric constant

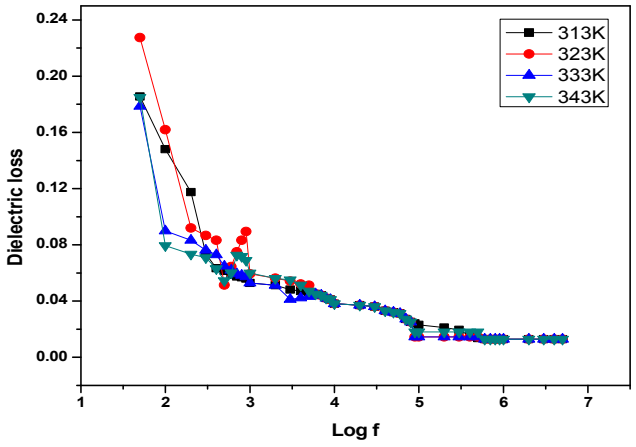

Figure 5. Log f Vs Dielectric loss

Conclusion

Single crystals of LH5SS were grown by slow evaporation solution growth technique. This material was found to crystallize in the noncentro symmetric space group of $P2_1$. Thermal studies infer good thermal stability of the material. The decomposition patterns were formulated based on the percentage weight losses. The variations of dielectric constant

as a function of frequency at different temperature are discussed. LH5SS posses very good laser damage threshold values and it is suitable for NLO device fabrication.

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