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Spectroscopic Investigation of Zinc Sulphamate – A Novel Non-Linear Optical Crystal

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Single crystals of zinc sulphamate were grown by slow evaporation solution growth technique at room temperature. Formation of the new crystal has been confirmed by powder and single crystal X-ray diffraction. The chemical composition of the crystal was revealed by energy dispersive X-ray analysis. The presence of functional groups in the crystal lattice has been qualitatively determined by FT-IR and FT-Raman analyses. The optical transmission spectroscopy (UV-visible) clearly evidences the suitability of this material for optical application. The non-linear optical characteristics of this material was explored by the second harmonic generation conversion efficiency.

Keywords: Non-linear optics, Optical devices, Materials.

INTRODUCTION

Growth of non-linear optical (NLO) single crystals with good quality initiates the development of many novel devices in the field of optoelectronics and optical communication such as optical modulators, optical data storage and optical switches[1,2]. The search for new materials with high optical non-linearities is an important task because of their practical applications in harmonic generation, amplitude and phase modulation, laser technology and other signal processing devices. The high second harmonic conversion efficiency and transparency in visible, ultraviolet region are required for various devices[3-5]. Most recent work has demonstrated that organic crystals can have very large non-linear susceptibilities compared with inorganic crystals, but their use is impeded by their low optical transparencies, poor mechanical properties, low laser damage thresholds and inability to produce and process large crystals[6]. The inorganic materials are widely used in these applications because of their high melting point, high mechanical strength and high degree of chemical inertness[7]. Mainly solution growth techniques have been applied for growing good quality crystals.

Sulphamic acid (H_2NSO_3H) (SA) is the mono-amide of sulphuric acid and is formed as orthorhombic crystal. It is highly stable and it can be kept for years without any change in properties. It is a strong inorganic acid, while mixing it with water it exihibits Zwitterionic form[8]. Owing to these advantages, JIS [Japanese industrial standard] has established this reagent as a standard substance for titrimetric analysis and the British analytical methods committee as well as IUPAC has also recommended the acid[9].

In this present work, a systematic investigation has been carried out on the growth of zinc sulphamate single crystals and the grown crystals are subjected to powder X-ray and single crystal X-ray diffraction, EDAX, FT-IR, FT-Raman, UV-visible-NIR and second harmonic generation efficiency studies.

EXPERIMENTAL

Synthesis: Saturated solution was prepared by dissolving required amount of sulphamic acid and zinc sulphate in double distilled water. The solution was stirred continuously using magnetic stirrer to achieve homogeneous mixing of solvent. The solution was then filtered using Whatmann filter paper to remove the suspended impurities. Then the solution is transferred to different crystal growth vessels and is kept in an undisturbed state. They are allowed to crystallize by slow evaporation at room temperature. Repeated recrystallization was done to improve the purity of the crystal. After a growth period of 15 days, good quality zinc sulphamate crystals were harvested.

Characterization studies: The grown crystals of zinc sulphamate were subjected to powder X-ray diffraction patterns using EX 2050 powder X-ray difractometer with CuK_α radiation to confirm its crystallinity. Single crystal X-ray diffraction was carried out using Enraf Nonius-CAD 4 diffractometer to determine the cell parameters and crystal structure. The EDAX analysis was done by INCA, oxford instruments to identify the elements present in the grown crystals. The FT-IR and

FT-Raman spectra were recorded using BRUKER: RFS spectrometer in frequency range 400-4000 cm^{-1} to analyze the presence of functional groups. The optical transmission spectrum was recorded by double beam UV-visible spectrophotometer in the range 200-800 nm covering the entire near ultraviolet, visible and NIR regions. The non-linear optical property was tested using Kurtz and Perry powder test.

RESULTS AND DISCUSSION

Powder X-ray diffraction analysis: In the present study, finely crushed powder of the sample was subjected to powder X-ray diffraction analysis. The sample was scanned over the diffraction angle range 20°-70° at a scan rate of 1 °/min. The XRD pattern with correspondingly indexed d spacing is shown in Fig. 1.

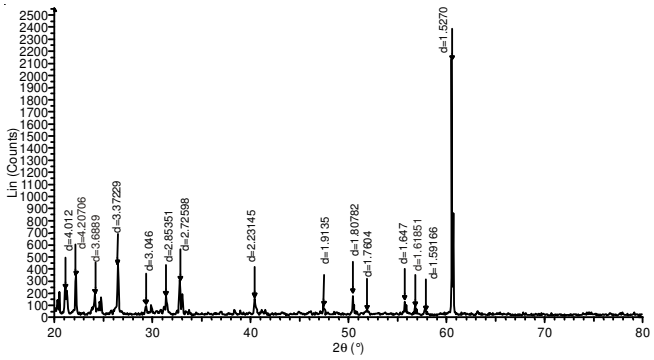

Fig. 1. Powder XRD pattern of zinc sulphamate

Sharp and well defined Bragg's peaks at specific 2θ angles confirm the crystalline nature of the synthesized compound.

Single crystal X-ray diffraction analysis: The titled material has been subjected to single crystal XRD employing Enraf Nonius- CAD 4 diffractometer. The single crystal XRD study reveals that the grown crystal belongs to tetragonal crystal system and the lattice parameters are a = 8.05 Å, b = 8.05 Å and c = 9.20 Å. The volume of the material is 596 Å. These values are compared with already reported value of sulphamic acid[10] crystals and are tabulated in Table-1.

Energy dispersive X-ray analysis: Quantitative energy dispersive X-ray analysis (EDAX) is the commonly used method for chemical analysis of materials. In this investigation the grown crystal was subjected to EDAX analysis to confirm the presence of elemental composition. The results are shown in Table-2.

TABLE-2
ELEMENTAL COMPOSITION OF ZINC SULPHAMATE

Element	App Conc	Intensity Corrn.	Weight (%)	Weight (%) Sigma	Atomic (%)
O	21.30	1.0002	38.25	1.06	67.12
S	6.45	0.8125	14.25	0.51	12.48
Zn	23.06	0.8722	47.50	1.11	20.40
Total	-	-	100.00	-	-

It is observed that about 20 percent of the total composition is formed by zinc ions which gave a strong evidence for the incorporation of zinc ions inside the sulphamic acid lattice. The recorded spectrum is shown in Fig. 2.

The distinct peak of zinc observed in the graph also indicates its presence inside the lattice. This confirms the presence of zinc and sulphonic groups.

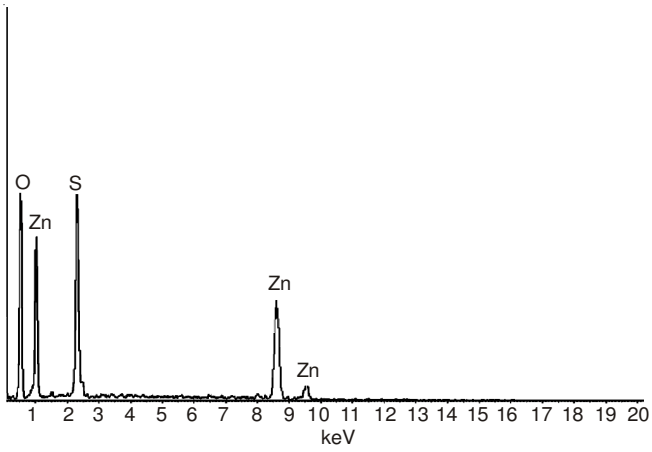

Fig. 2. EDAX spectrum

Fourier transform infrared spectroscopy analysis: Fig. 3 shows the recorded spectrum of FT-IR.

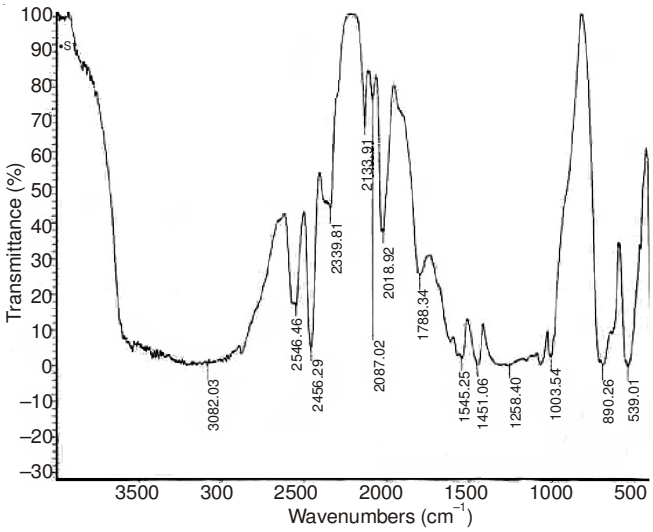

Fig. 3. FT-IR spectrum

The band at 3082 cm^{-1} corresponds to asymmetric stretching mode of N-H. The presence of bands between 2546-2133 cm^{-1} is mainly due to N-H stretching[11]. The peaks at 1545 and 1451 cm^{-1} are due to degenerate NH_3^+ deformation and asymmetric stretching of NH_3^+ mode, respectively. Peak at 1256 cm^{-1} corresponds to N-H…S bond and 1003 cm^{-1} is due to NH_3^+ rocking. This rocking mode vibration confirms the

TABLE-1
CELL PARAMETERS OF ZINC SULPHAMATE SINGLE CRYSTALS

Sample	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)	Volume (A^3)	Crystal System
Sulphamic acid	8.078	8.116	9.268	90	90	90	607.619	Orthorhombic
Zinc sulphamate	8.05	8.05	9.20	90	90	90	596.6	Tetragonal

zwitterionic nature[12]. N-S stretching occurs at 690 cm^{-1} and SO_3^- deformation takes place at 539 cm^{-1}.

FT-Raman analysis: The recorded FT-Raman spectrum was shown in Fig. 4. The presence of functional groups was further confirmed by Raman spectrum. The vibrational assignments are tabulated in Table-3.

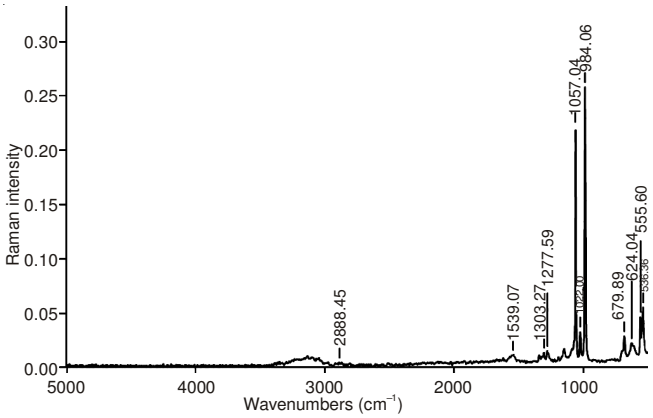

Fig. 4. Raman spectrum of zinc sulphamate

TABLE-3
VIBRATIONAL ASSIGNMENTS OF ZINC SULPHAMATE

Wave number (cm^{-1})	Vibrational assignments
2888	sym. NH_3^+ stretching
1539	degen. NH_3^+ deformation
1303	degen. SO_3^- stretching
1277	N-H… S bond
1057	sym. SO_3^- deformation
1022	NH_3^+ rocking
984	NH_3^+ rocking
679	N-S stretching
555	SO_3^- deformation
536	SO_3^- deformation

UV-visible-NIR studies: UV-visible spectra give limited information about the structure of the molecule because the absorption of UV and visible light involves promotion of the electron in the σ and π orbitals from the ground state to higher energy states[10]. A non-linear optical material can be of practical use only if it has wide transparency window. To determine the transmission range and hence to know the suitability of single crystals for optical applications the UV-visible transmission spectrum was recorded employing a double beam UV-visible spectrophotometer (Fig. 5).

It is evident that there is no absorption of light to any appreciable extent in the visible region of electromagnetic spectrum. The lower cut off wavelength is around 200 nm and the crystals possess a better transparency between 200 nm and 800 nm. This shows that the crystal is good enough for the second harmonic generation of Nd-YAG laser of wavelength 1064 nm. It is an important requirement for non-linear optical materials having non-linear optical applications[13].

Non-linear optical studies: Second harmonic generation property of the grown zinc sulphamate crystal was examined by Kurtz and Perry powder technique. The crystal was powdered and sandwiched between the glass slides. The fundamental beam of 1064 nm from Q-switched Nd:YAG laser was focused on the slides. The emission of green radiation of wavelength

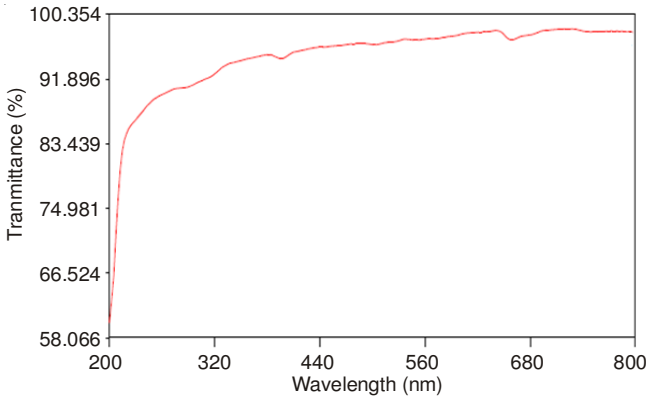

Fig. 5. Transmittance spectrum

532 nm confirms the second harmonic generation in the crystal. The SHG efficiency is found to be 0.89 times that of the standard KDP crystal.

Conclusion

Single crystals of zinc sulphamate has been grown successfully by slow evaporation technique. Powder XRD pattern confirms the crystallinity of the grown crystal. Single crystal XRD studies confirm the newly formed crystal. The incorporation of zinc ions inside the SA lattice has been clearly evidenced by energy dispersive X-ray analysis. The FT-IR and FT-Raman spectra show the presence of amine and sulphonic groups. The UV-visible studies showed that the transparent window is good enough in the visible region which is a desirous property for this material for non-linear optical applications. The SHG nature of the crystal was tested by Kurtz and Perry powder testing which attributes to the non centrosymmetric nature of the crystals. Its efficiency is found to be 0.89 times that of the standard KDP crystal. All the above strongly attributes zinc sulphamate, a novel material for non-linear optical applications.

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