Synthesis, Crystal Growth and Characterization of Serine Zinc Acetate an Organic Nonlinear Optical material by Slow Evaporation Method

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Abstract

Optically good quality single crystal of Serine Zinc Acetate (SZA) was grown by the method of slow evaporation and using a solvent of water. The value of cell parameters was obtained by single crystal XRD study. The various functional groups of molecules present in SZA were identified from FTIR studies. The optical behaviour of the grown crystal was analysed through UV-VIS-NIR spectral studies and the material SZA was found to have wide range of transparency in the visible region. The Vickers micro hardness study revealed the hardening nature of the grown material. Thermal stability of SZA was confirmed using thermo gravimetric and differential thermal analyses. The NLO activity of the grown crystal was tested by Kurtz-Perry powder technique. Copyright © VBRI Press.

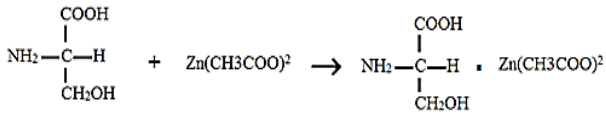
Keywords: Single crystal XRD, FTIR, UV-VIS-NIR, micro hardness, thermal, NLO.

Introduction

Some polar organic crystals show second order nonlinear optical property that far exceeded those of the conventional materials has led to the synthesis and evaluation of a wide range of possibly useful solids [**1**]. Nonlinear optical media help us to generate frequencies that are not available through frequency conversion technique. Organic amino acid crystals possess high NLO efficiency because of their non-centro symmetric space group and chiral carbon atom [**2**]. Second harmonic generation can be improved by large delocalizedπ-electron with donor and acceptor groups. Amino acids contain carboxyl acid COO^- group (a donor) and NH_2^+group (acceptor) with them. In this amino acid family L-Serine is one of the organic amino acids and exists in a zwitter ionic form, which shows a good nonlinear effect, so they have been reported in current years. Here, we present a report on synthesis and growth, XRD, FTIR, transmission and absorption, micro hardness, TGA/DTA and nonlinear optical studies of SZA single crystals.

Materials and methods

The commercially available serine and zinc acetate (AR grade) salts are taken in equal molar ratio have been used to synthesise the SZA single crystals. The solution was prepared using distilled water. The scheme of the reaction is shown below.



Initially serine and zinc acetate was dissolved in distilled water and have continuous stirring for one hour. The final product is filtered by Whatman filter paper and kept in a beaker. The solution was placed in undisturbed position. After ten days, colourless, single crystal of dimension 3x3x1 mm^3 was obtained by slow evaporation of the prepared solution. **Fig. 1** shows the photograph of as grown crystal of SZA.

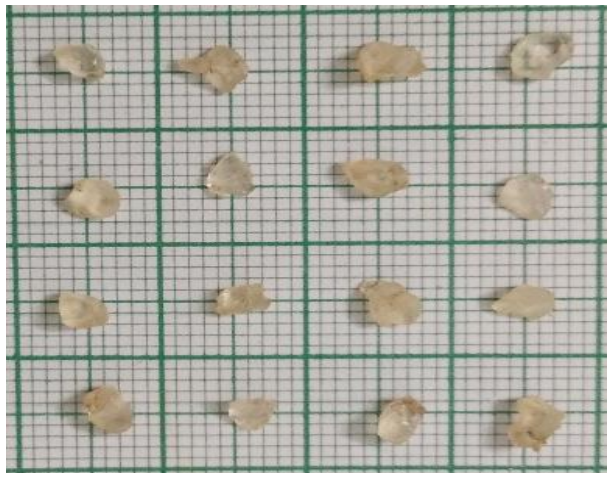


Fig. 1. Photograph of SZA crystals.

Result and discussion

Single crystal XRD studies

The single crystal X-ray diffraction analysis of grown crystal was carried out using the ENRAF NONIUS CAD4 automatic X-ray diffractometer. The structure was solved by the direct method and refined by the full matrix least square technique using the SHELXL program. The collected cell parameter values are given by a = 5.532Å, b = 9.52Å, c = 8.421Å and α = γ = β = 90°, the cell volume V = 434.52Å^3. The data obtained from single crystal XRD confirms the grown crystal belongs to orthorhombic system.

FTIR analysis

The KBr pellet technique is used to record the Fourier Transform Infrared spectrum of the grown crystals in the region 450 - 4000 cm^{-1} by using Bruker IFS 66V model spectrometer. **Fig. 2** shows the characteristic peaks observed in the FTIR spectrum of SZA.

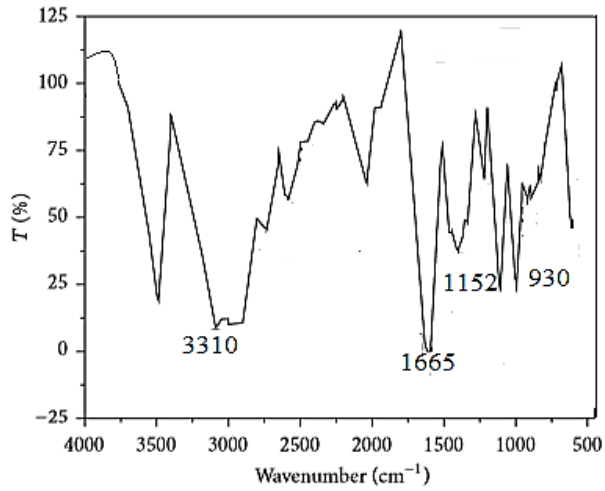


Fig. 2. FTIR Spectrum of SZA.

The presence of NH_2 group in the FTIR spectrum shows a strong band around 3310 cm^{-1} and protonated by the carboxyl group (COOH) giving hydrogen bonding interaction between NH_2^+ and COO^-. The broad envelop band around 3000 cm^{-1} to 2000 cm^{-1} is due to superimposed O-H and NH_3^+ stretching vibrations. The C=O stretching mode corresponds to the absorption peak at 1665 cm^{-1}. The asymmetric coupled vibration of acetate and serine had an absorption peak between 930 cm^{-1} and 1152 cm^{-1}.

UV-VIS -NIR spectral studies

The absorbance and transmission series of the grown crystal was documented by using Lambda-35 Spectrometer in the wavelength assortment of 200 nm to 1100 nm. **Fig. 3** shows the recorded spectrum of SZA material.

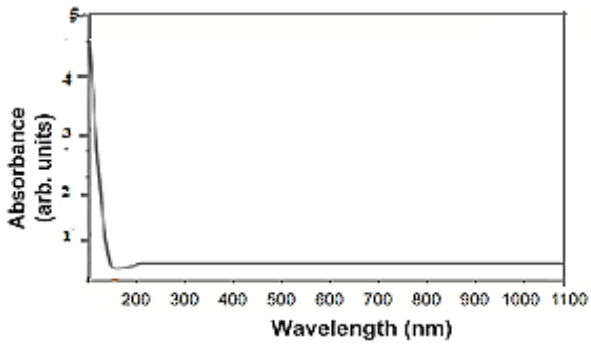


Fig. 3. Absorbance Spectrum of SZA.

The absorbance reduced between the wavelength 250nm and 1100 nm is due to its good optical behaviour. The crystal had lesser cut-off wavelength about 245 nm, which confirmed the absence of any overtones and absorbance due to electronic transitions.

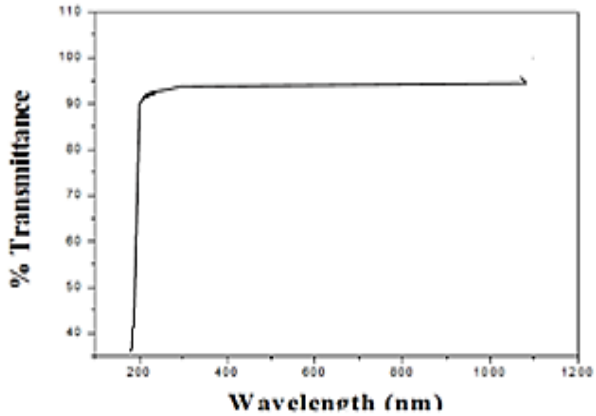


Fig. 4. Transmittance Spectrum of SZA.

A graph of percentage of transmission versus wavelength is shown in **Fig. 4**. The optical spectrum of SZA shows a good transmittance in the visible region. The spectrum of SZA crystal shows that there is no absorption in the wavelength range from 300 nm to 1400 nm. The grown SZA crystal has a UV cut off wavelength about 190nm. This makes SZA materials suitable for UV tuneable lasers and second harmonic generations [**3**].

Micro hardness studies

Micro hardness test is the suitable method to find the mechanical property of the materials. The hardness of grown crystal has been evaluated using Vicker's micro hardness tester. Smooth surface of the crystal was selected and then subjected to static indentation period of 5s to estimate the hardness nature of the grown SZA material. The indented impressions were approximately square. The following relation is used to calculate the micro hardness number H_V.

$$H_V = \frac{1.855P}{d^2}$$

where P is the applied load in Kg and d is the average diagonal length of the indentation mark in mm. **Fig. 5** shows the hardness of SZA material as a function of load Vs hardness number.

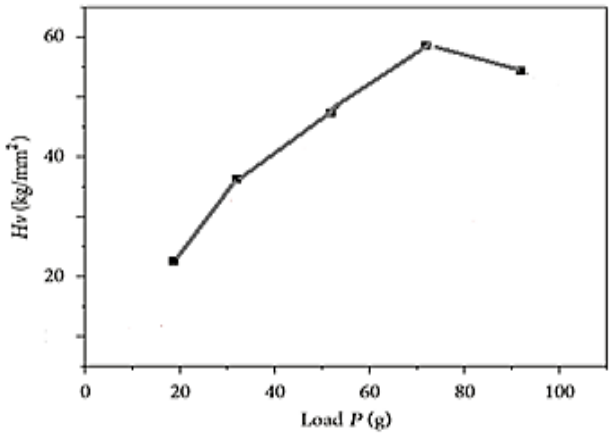


Fig. 5. Micro hardness plot of SZA.

From the graph, it clear that the hardness number increases with the increase in load upto70 g. The load increased above 70g develops cracks and hardness number decreases with further increase in load. The work hardening coefficient of SZA was found to be less and it is fit in hard material category [**4**].

Thermal analysis

Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) of the sample was carried out by using the TGA Q500 TA instrument. The TGA was carried out in atmosphere of nitrogen and the heating rate of 20^0C per minute. The temperature range was 30^0C to 600^0C.

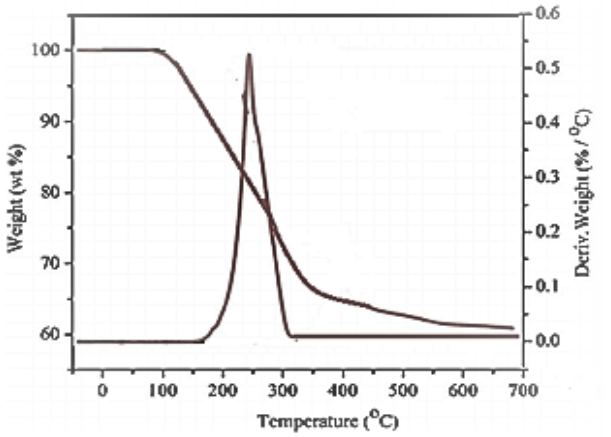


Fig. 6. TG-DTA Analysis of SZA.

The material is stable up to 115^0C and the weight loss starting from 115^0C to 350^0C as shown in **Fig. 6**. In DTA curve, the peak at 255^0C indicates the melting point of the grown sample. The melting point of serine is 228^0C but the endothermic peak observed at 255^0C confirms the addition of zinc acetate.

SHG efficiency test

The NLO efficiency of the crystal was estimated by using Kurtz and Perry powder method. The powdered sample was focused by fundamental beam of Q-switched Nd:YAG laser operating at 1.06 nm and generating pulses of duration 35 ns and 10 Hz repetition rate. The SHG is confirmed by emission of green radiation from the sample. The well-known NLO crystals are taken as the reference materials and the conversion efficiency of SZA is compared. The SHG efficiency of SZA was 1.1 times greater than the standard KDP crystal.

Conclusion

A single crystal of serine zinc acetate (SZA) was successfully grown by using the slow evaporation solution growth. The single crystal X-ray diffraction analysis confirmed the structure of the crystal. The minimum absorption in the entire visible region and lower cut off wavelength near 190 nm indicates its applicability to NLO material. The various functional groups of SZA have been recognized from FTIR spectral analysis. The thermo gravimetric analysis confirms the thermal stability of the SZA up to 115^0C and the addition of zinc acetate increases the stability of the grown crystal. The hardness test showed that the crystal is unchanging up to 70g. The Kurtz and Perry powder test confirmed that SHG efficiency of SZA is 1.1 times greater than the KDP.

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