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Growth of non linear optical zinc thiosemicarbazide sulfate single crystal and its studies on FT-Raman, XRD, mechanical and dielectric studies

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Abstract: Single crystals of zinc thiosemicarbazide (ZTSCS) sulfate have been grown from solution growth method using slow evaporation technique. The functional groups, structure, mechanical and dielectric behavior have been verified by FT-Raman, powder X-ray diffraction, Vicker's microhardness and dielectric studies. The functional group present in the title compound was found by FT-Raman studies. The grown crystal was subjected to powder XRD which confirmed that the crystal has monoclinic crystal system. The hardness of the ZTSCS was studied by Vicker's hardness tester. The dielectric measurements on the powdered sample have been carried out and the variation of dielectric constant and dielectric loss at different frequencies of the applied field has been studied. The results of all the characterization are discussed in detail.
Keywords: Slow evaporation technique, FT-RAMAN studies, Vicker's hardness tester, dielectric measurements.

1. Introduction

In the recent past, extensive investigations are being carried out on non linear optical materials due to their potential applications in optoelectronics, telecommunications and optical storage devices [1-6].Organic NLO materials have high non-linearity and wide transparency range [7,8]. Mechanical and thermal stabilities are found to be high for inorganic crystals. These difficulties were overcome by semiorganic NLO material. Hence semiorganic crystals with combined properties of organic and inorganic crystals have attracted the attention of researchers [9]. Semiorganic compounds illustrates the following important features (i) dipolar structure composed of an electron donating and electron accepting group; (ii) the concentration from the delocalized π- electron belonging to the organic ligand results in high nonlinear optic and electro-optic coefficients in the semiorganic crystal; (iii) the organic ligand is ionically bonded to metal ion give improved mechanical and thermal properties; (iv) exhibit wide transparency range, chemical stabilities and bulk crystal morphologies [10]. In the past few years, much attention has been paid to the research of nonlinear optical crystal based on thiosemicarbazones because of their biological activities and their second harmonic efficiencies [11].Thiosemicarbazide has been shown to be a good ligand for a range of metals including zinc, cadmium, mercury and nickel [12,13]

Growth, FT-RAMAN, XRD, mechanical and dielectric studies of non linear optical zinc thiosemicarbazide sulfate single crystal is analysed in this paper. The growth, vibrational, structural, mechanical and dielectric properties of ZTSCS single crystals were studied and reported.

2. Experimental

ZTSCS crystal was grown by dissolving AR grade of zinc sulfate heptahydrate and thiosemicarbazide in an equimolar ratio in an aqueous medium. Calculated amount of reactants were completely dissolved in double distilled water and stirred well by using magnetic stirrer to ensure a homogenous solution and then the solution was filtered into borosil beaker using Whatmann filter paper. Finally the beaker were closed with a perforated cover and kept in a dust free atmosphere for crystallization.

The growth was initiated due to slow evaporation of the solvent. A transparent, needle shaped good quality crystals with dimension of 16 X 4 X 3 mm³ were harvested after a period of about 165 days. The as grown single crystals of zinc thiosemicarbazide sulfate are shown in figure 1.

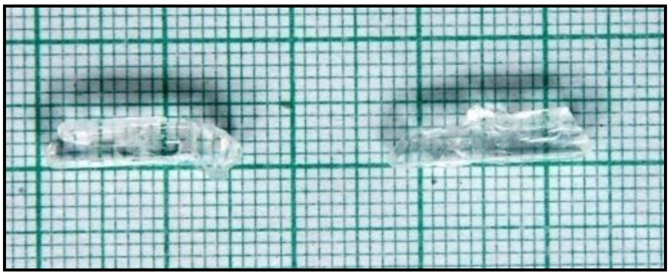

Fig.1 Photograph of ZTSCS Crystal

3. Results and Discussion

3.1 FT-Raman analysis

The FT-Raman spectra of title compound were used to confirm the functional groups present in the sample. The recorded FT-Raman spectrum is given in figure.2.The observed bands and their assignments are listed in table 1.

The strong Raman peaks shows in the region from 491 cm^{-1} to 102 cm^{-1} are due to lattice vibrations [14, 15]. The presence of sulfate ion is confirmed by the peak at 950 cm^{-1} and 451 cm^{-1} [16].The peak at 1593 cm^{-1}, 720 cm^{-1} and 618 cm^{-1} are due to presence of COO^- asymmetric, scissoring and bending mode of vibrations within the sample. The presence of band at 1409 cm^{-1},1011 cm^{-1}, 885 cm^{-1} and 667 cm^{-1} shows C=S, C-N,C-C-N symmetric stretching and O-C=O in plane deformation respectively. The CH_2 deformation, scissoring, twisting and rocking vibration are lying in the range 1440 cm^{-1}, 1345 cm^{-1}, 1323 cm^{-1} and 788 cm^{-1} [17]. The NH_2 asymmetric stretching and NH_2^+ symmetric deformation are found at 3384 cm^{-1} and 1563 cm^{-1}. The C=O ion carboxyl amino acid band occurs at 1643 cm^{-1}. The peak at 2887 cm^{-1} corresponds to N-H hydrogen band oscillations. NH_3^+ asymmetric and symmetric stretching are found in the wavenumber 3054 cm^{-1} and 2931 cm^{-1} respectively.

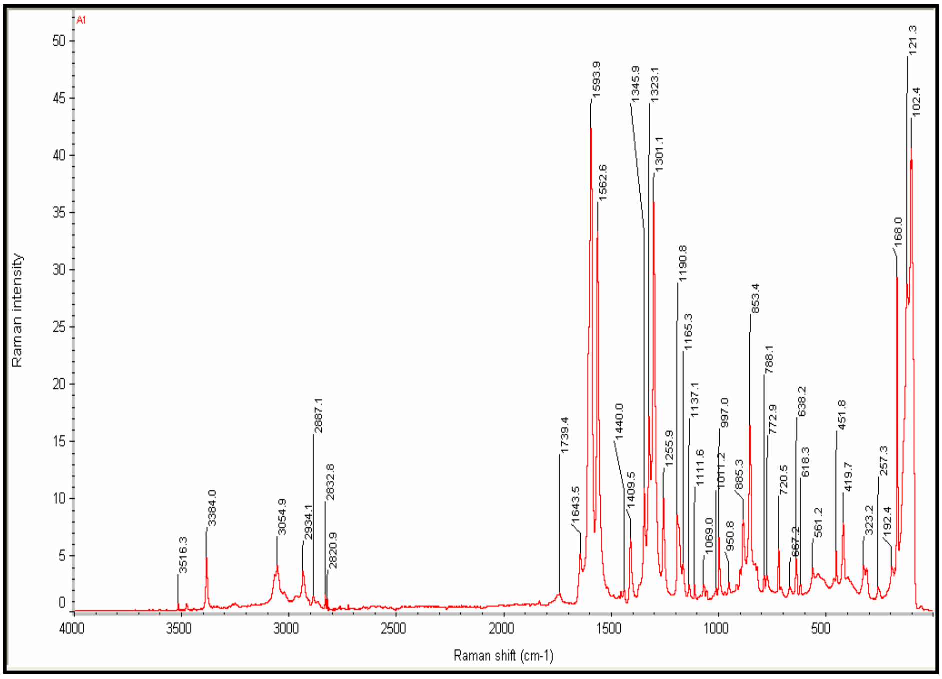

Fig.2 FT-Raman spectra of ZTSCS crystal

Table 1.FT-Raman wavenumbers (cm^{-1}) of ZTSCS

Raman wavenumber (cm^{-1})	Mode Assignments
3384	NH_2 asymmetric stretching
3054	NH_3^+ asymmetric stretching
2931	NH_3^+ symmetric stretching
2871	N-H hydrogen bonded oscillation
1643	C=O ion carboxyl amino acid band
1593	COO^- asymmetric stretching
1563	NH_2^+ symmetric deformation
1440	CH_2^+ deformation
1409	C=S symmetric stretching
1345	CH_2 scissoring
1323	CH_2 twisting
1137	NH_3^+ rocking
1011	C-N stretching
950	Presence of sulfate ion
885	C-C-N symmetric stretching
788	CH_2 rocking
720	COO^- scissoring
667	O-C=O in plane of deformation
618	COO^- bending
451	Presence of sulfate ion
419,332,257,192, 168,121 and 102	Lattice vibrations

3.2 Powder XRD

The crystalline quality of the ZTSCS crystals and their cell dimensions were detected by using PHILIPS X-ray diffractometer with Cu-Kα radiation of wavelength 1.5405 Å in the 2θ range 10^0-80^0 at a rate of 1^0 per minute. The powder XRD patterns of zinc thiosemicarbazide sulfate crystals are shown in figure 3.Usinng XRDA and unit cell software the peak are indexed and the lattice parameter values are evaluated. The unit cell parameters obtained are a = 11.36 Å, b = 16.10 Å, c = 5.565 Å, α = β = 90˚, γ = 94.1˚ and V = 1016.05 $Å^3$. It is confirm that the grown crystal belongs to class of monoclinic crystal system.

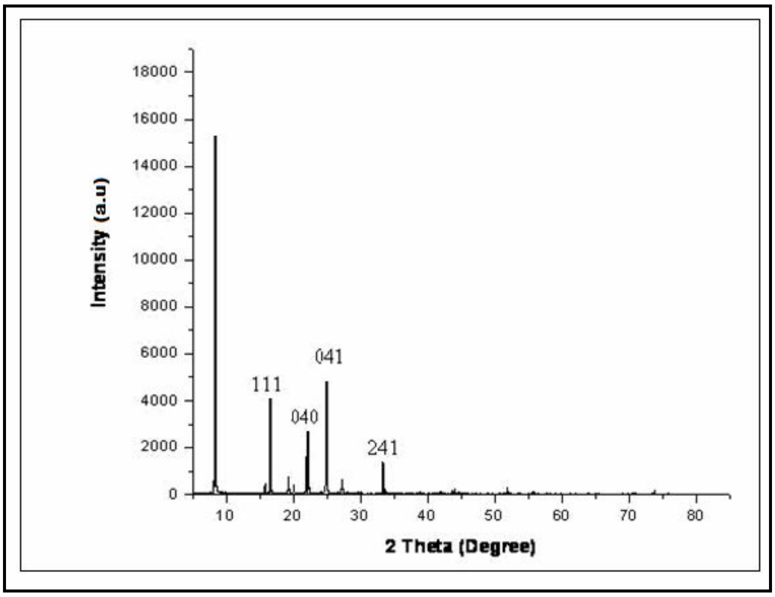

Fig.3. Powder XRD pattern for ZTSCS crystal

3.3 Mechanical properties

Mechanical properties of the grown zinc thiosemicarbazide (ZTSCS) sulfate crystals were studied using HMV-2T Vickers micro hardness tester. The Vickers micro hardness values were calculated from the standard formula.

$H_V=1.8544P/d^2$ ………. Kg/mm^2

Where, P-is the indenter load in (Kg) and d-is the diagonal length of the impression in (mm).The calculated Vickers hardness values for zinc thiosemicarbazide sulfate crystal as a function of load as shown in figure 4 from which is observed that the hardness increases with the increase of load. In order to find work hardening coefficient n of the grown crystal, another graph was drawn between logarithmic values of load and diagonal length of indentation figure 5. From Meyer's law $p = ad^n$ connecting the relationship between applied load and diagonal length of the indentation, work hardening coefficient or the Mayer index was calculated. Here 'a' is the constant for the given material. The calculated work hardening coefficient is n=1.7. According to Onitsch and Hanneman 'n' should lies between 1 and 1.6, then the grown crystal will be a hard material and it is more than 1.6 for soft materials [18, 19]. Since the calculated work hardening coefficient 'n' is suggested that the grown ZTSCS crystal comes under the category of soft material.

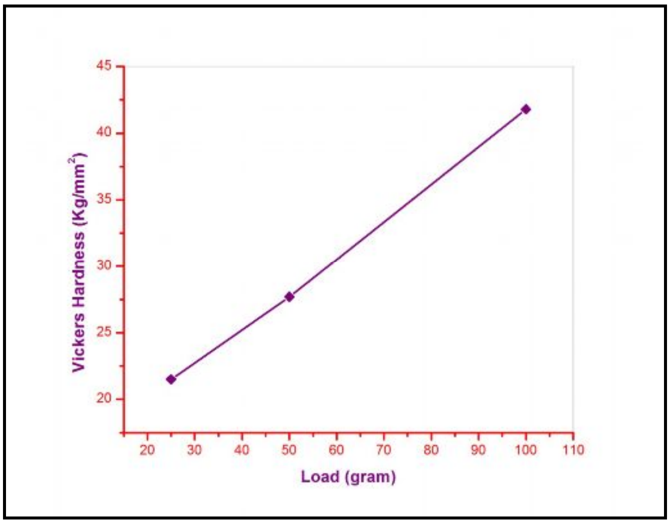

Fig.4. Variation of Load P with H_V

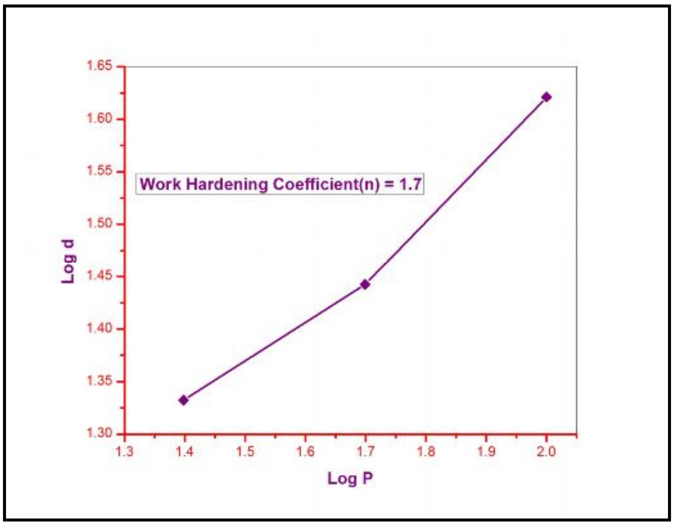

Fig.5. Variation of Log P with Log d

3.4 Dielectric studies

Dielectric properties are correlated with the electro optic property of the crystals [20]. The dielectric responses of the ZTSCS crystals were studied by LCR HIOKI 3532 HI TESTER from the frequency range 50

Hz to 5 MHz in the temperature range from 313 K to 353 K. The powder ZTSCS sample was shaped as pellets of length 13.2 mm, breadth 7.83 mm and thickness 2.78 mm. Then these pellets were thinly coated with high purity air dry silver paste to make them into a parallel plate capacitor. The dielectric constant was calculated using the relation,

$$\varepsilon_r = \frac{Ct}{A\varepsilon_0}$$

Where, C is the capacitance, t is thickness of the sample, ε_0 is the permittivity of the free space (8.854×10^{-12}F/m) and A is the area of the cross section of the sample.

Figure 6 and 7 shows the variations of dielectric constant and dielectric loss of ZTSCS crystal at different temperatures ranging from 50 Hz to 5MHz as a function of frequency. From the figure 6, it is evident that the dielectric constant decreases slowly with the increase in frequencies and attain saturation higher frequencies at all the temperatures. This may be due to the contributions of all the four polarisations such as electronic, ionic or atomic, dipolar or orientation and space charge or interfacial polarization are predominant at lower frequency region and its low value at high frequencies may be due to the loss of significance of these polarisations gradually [21, 22]. The low dielectric loss implied that the sample possesses good optical quality with lesser defects which is the excellent property for NLO applications.

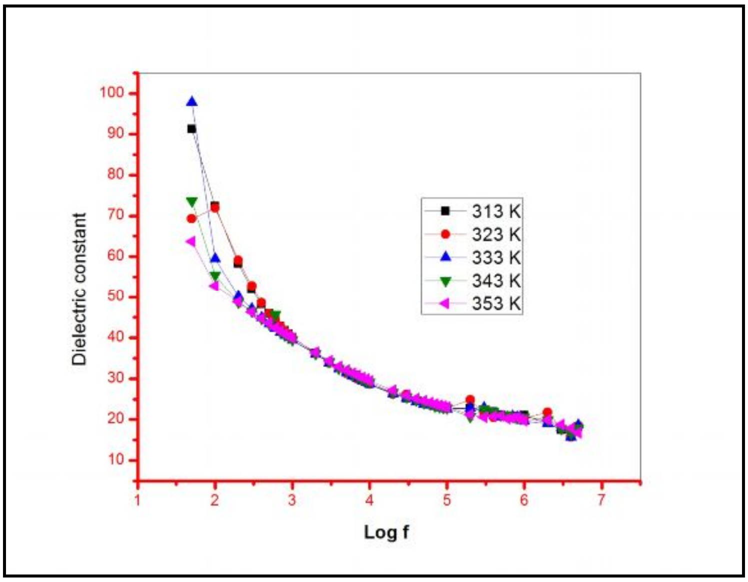

Fig.6. Plot of log frequency with dielectric constant at different temperature

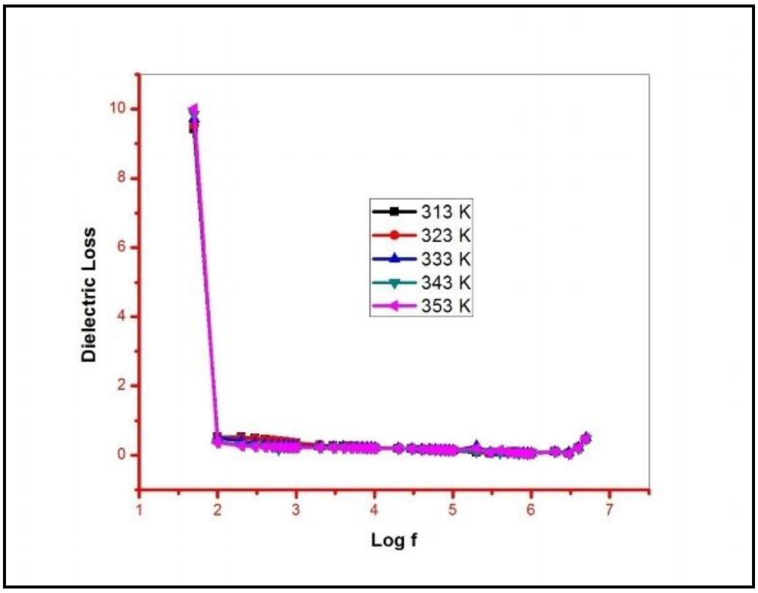

Fig.7. Plot of log frequency with dielectric loss at different temperature

Conclusion

A zinc thiosemicarbazide sulfate crystal was successfully grown by slow evaporation technique. The molecular vibrations are confirmed through the FT-Raman spectral analysis. The powder X-ray diffraction studies reveals that the monoclinic structure and crystallinity of the grown crystal. From the mechanical microhardness test, it was noticed that H_V increases with increase of load and the value of Mayer's index shows that the ZTSCS crystal belongs to the category of soft material. The dielectric measurements indicate that the grown crystal is suitable for NLO applications. The above results show that the ZTSCS crystal is a potential candidate for opto-electronic devices.

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