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GROWTH AND CHARACTERIZATION OF ALANINE DOPED ZINC TRIS THIOUREA SULPHATE SINGLE CRYSTAL

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ABSTRACT
An attempt has been made in the present work to grow doped crystal of zinc tris thiourea sulphate from aqueous solutions, precursors mixed in proper proportions. The X-ray diffraction measurements indicate that the grown crystals belong to orthorhombic structure. They possess a wide optical transmission window which is suitable for NLO applications.
Keywords: Nonlinear, X-ray diffraction, FT-IR, UV-Visible, ZTS

INTRODUCTION

Research is focused on new types of NLO materials which combine the advantages of organic and inorganic materials called semi organic materials. It is also interesting to observe that thiourea is an inorganic matrix modifier due to its large dipole moment and its ability to form an extensive network of hydrogen bonds. The Centro-symmetric thiourea molecule, when combined with inorganic salt yield noncentro-symmetric complexes, which has the NLO properties.[1-6] To improve the optical property of ZTS dopant alanine has been added and its influence on the growth and properties are studied in the present work.

EXPERIMENTAL

The recrystallized salts of Zinc Tris Thiourea Sulphate doped with alanine are used in the present crystal growth experiment. The ZTS seed crystals were prepared by dissolving analar grade thiourea and ZTS heptahydrate in equimolar ratio 3:1 in distilled water. The synthesized material was further purified by repeated recrystallization and it was used for the growth of ZTS crystals. The structural formula for ZTS crystals is as follows:

$$3\,CS\,(NH_2)_2 + ZnSO_4 \rightarrow Zn\,[CS\,(NH_2)_2]_3\,SO_4$$

Solubility

The solubility of the solute can be determined by dissolving the solute in the solvent maintained at a constant temperature with continuous stirring. The solubility curve can be plotted from the amount of solute dissolved and temperature by repeating the measurements for different temperatures. The solubility curve of ZTS crystal is shown in Figure-1.

The ZTS solution was prepared in water and maintained at 30°C with continuous stirring to ensure homogeneous temperature and concentration. On reaching saturation, the content of the solution was analysed gravimetrically. This process was repeated for every 5° C in water from 30° to 60° C.

Growth

The calculated amount of ZTS was added to double distilled water according to the solubility data and finally the whole solution was mixed with continuous stirring for 3 hours using magnetic stirrer and to obtain a homogeneous mixture. The completely dissolved solution was filtered using Whattman filter paper to remove the suspended impurities and allowed to crystallize by slow evaporation method at room temperature for about 45 days. Finally well-defined single crystals of ZTS was obtained. The photograph of grown crystal is shown in Figure-2.

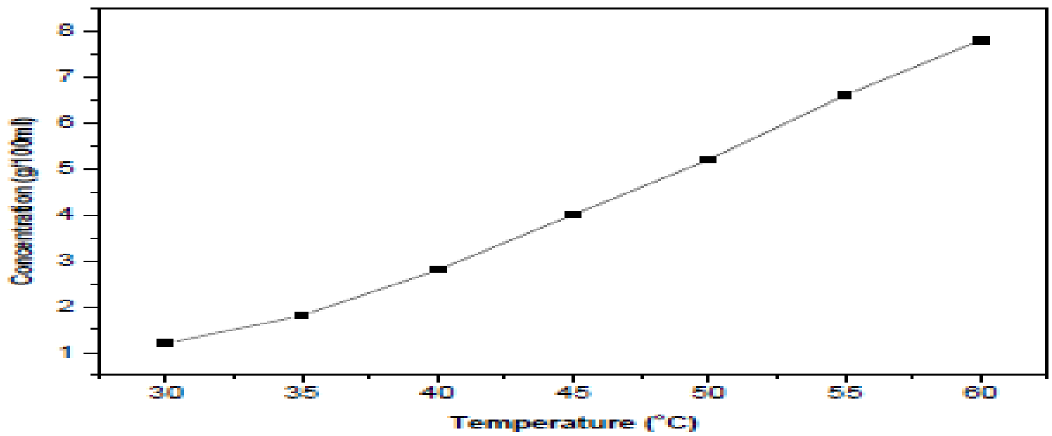

Fig.-1: Solubility curve for alanine doped ZTS crystal

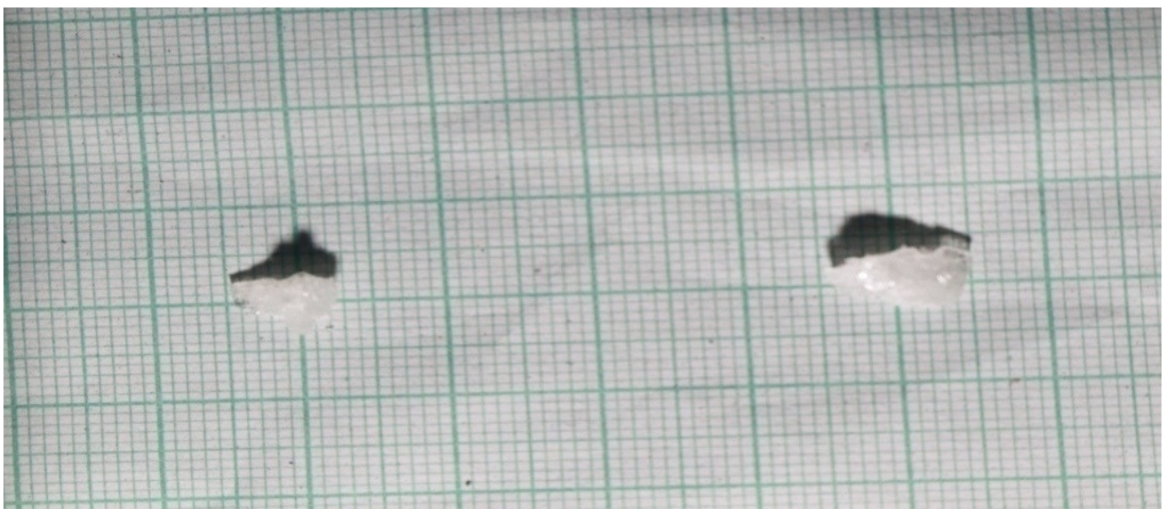

Fig.-2: Photograph of grown crystals of alanine doped ZTS Crystal

The saturated solution of ZTS was prepared in accordance with the solubility data by dissolving thiourea and zinc sulphate in the stoichiometric ratio 3:1 in double distilled water. Saturated solution of ZTS was thus prepared at room temperature and the solution was filtered. To this 2wt% of alanine was added to the solution. The solution was constantly stirred using magnetic stirrer for a day to avoid co-precipitation of multiple phases. The stirred solution was filtered and then allowed to evaporate at room temperature (30k). In the period of 30-45 days, seed crystals of ZTS were formed due to spontaneous crystallisation. Good shaped seed crystals were selected to grow bulk sized crystals. Crystals having dimension up to 10x10x5 mm^3 was harvested in a period of 50-60 days.

RESULTS AND DISCUSSION

Single crystal XRD Analysis

The single crystals of Zinc Tris Thiourea Sulphate doped with alanine were subjected to single crystal X-ray diffraction analysis using Bruker Smart Apex duo single crystal X-ray diffractometer to determine the lattice parameters and space group. X-ray diffraction (XRD) is a powerful non-destructive technique for characterizing crystalline materials. Single crystal X-ray diffraction is an analytical technique in which X-rays are employed to determine the actual arrangement of atoms within a crystalline specimen. XRD is employed for finding unit cell parameters, space groups; three-dimensional co-ordinates of atoms in the unit cell and mean thermal motion amplitudes of atoms in the unit cell.[7-14] Accurate measurements of intensities of reflections of Miller indices within a specified reciprocal radius is needed to find the structure, while unit cell parameters depend only on direction of reflections. For single-crystal work, the specimen should be smaller than cross section diameter of the beam. Larger crystals can be cut down to proper smaller crystals that contain strong diffracting elements. The monochromatic X-rays incident on a plane of single crystal is diffracted according to Bragg's law. The intensity of the diffracted rays depends on the arrangement and nature of atoms in the crystal. Collection of intensities on a full set of planes in the crystal contains the complete structural information about the molecule. With the set of space groups, molecular structure of the crystalline solids and miller indexing the different faces of the crystal are possible. Unit cell parameter is simply the dimension of the basic molecular brick within which the molecules are arranged within the unit cell. All the geometrical features of molecules may be obtained from coordinates. From single crystal XRD it is observed that alanine doped ZTS crystals belong to orthorhombic crystal system with cell parameters cell volume V = 665.7015 $Å^3$ a=7.28Å, b=11.56Å, c=15.63Å.[15]

Fourier Transform Infra Red Analysis

In order to find the presence of various functional groups and to identify the molecular structure of alanine doped ZTS spectral study was carried at room temperature. The recorded spectrum of ZTS is shown in Fig. 3. The spectral bands were interpreted and compared with standard spectra of the functional groups. It is observed that the broad envelope between 2508cm^{-1} and 3081cm^{-1} is due to overlapping of NH_3 and CH stretching modes. The symmetric and asymmetric N-C-N stretching vibration at 1417cm^{-1} of thiourea is shifted to 1510 cm^{-1} respectively. S-O stretching is observed at 608cm^{-1}. NH_2 stretching vibration at 3265 cm^{-1} is observed confirming the presence of alanine at 404 cm^{-1}. S-C-N symmetric bending is also observed.[16-22]

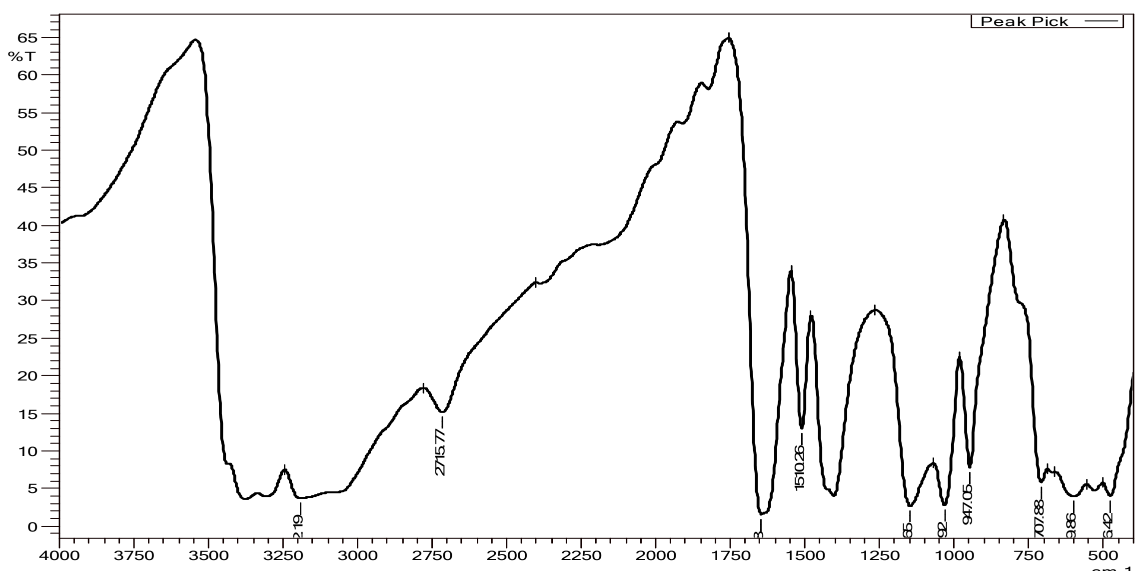

Fig.-3: FTIR Spectrum of alanine doped ZTS crystal

UV-Visible Spectral Analysis

The optical absorption spectrum plays a vital role in identifying the usefulness of a nonlinear material in the visible and UV regions. The UV-Vis-NIR absorption spectrum was recorded for the ZTS crystal in the wavelength region of 200-1200 nm using a Varian Carry – 5E UV-Vis spectrophotometer. UV-Vis-NIR spectroscopy might be defined as the measurement of the absorption or emission of radiation associated with changes in the spatial distribution of electrons in atoms and molecules.[23-25] In practice, the electrons involved are usually the outer valence or bonding electrons, which can be excited by the absorption of UV or visible or near IR radiation. The absorbance is very less in the UV and the entire visible region, which is an interesting observation in these materials. All the grown crystals exhibit wide transmission window in the visible and NIR regions. This enables them to be potential candidates for opto-electronic applications. A lower cut-off wavelength of 280nm is observed in the case of alanine doped ZTS crystals, which is a desirable property of the material for NLO applications. The ZTS optical absorption spectrum is shown in Figure-4.

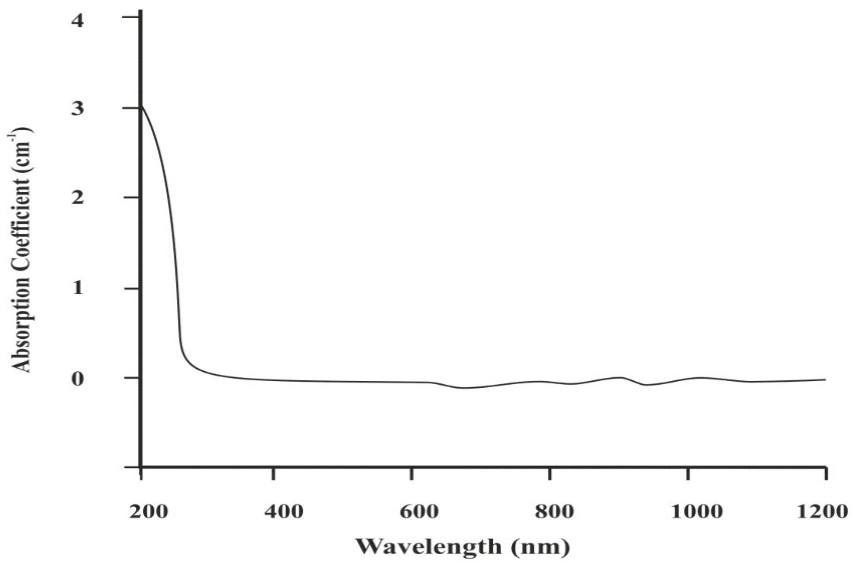

Fig.-4: The optical absorption spectrum of alanine doped ZTS crystal

Kurtz and Perry SHG test

The SHG efficiency of grown samples was measured by using the Kurtz powder technique. Second harmonic generation (SHG) is a nonlinear optical process that results in the conversion of an input optical wave into an output wave of twice the input frequency. In this technique, the grown crystals were grounded into fine micro crystalline powder and densely packed between two transparent glass slides. The fundamental beam 1064nm from Q-switched Nd: YAG laser was made to fall normally on the crystalline powder. This important nonlinear property of non-centrosymmetic crystals are called second harmonic generation (SHG) and this phenomenon and the materials in which it occurs are the subject of intense study.[26-29] The bright emission of green light from the alanine doped ZTS samples (λ=532 nm) confirms the second harmonic generation behavior of crystals. The light emitted by the sample was detected by photo diode detector and oscilloscope assembly.

CONCLUSION

Single crystals of alanine doped ZTS single crystals were grown by slow evaporation technique in a period of 45 days. XRD analysis confirms that the grown crystals belong to orthorhombic system. Functional groups and the modes of vibrations have been identified by FTIR spectral analysis. The minimum absorption in the entire visible range and lower cut-off wavelength near 260 nm shows the suitability of this material for NLO applications. The NLO property analyzed with Kurtz and Perry Powder technique confirms the grown crystal is nonlinear in nature.

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